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**SYNTHESIS, OPTIMIZATION, AND
CHARACTERIZATION OF BIOMASS GRAPHENE AND
ITS NANOCOMPOSITES FOR ELECTROCHEMICAL
ENERGY STORAGE DEVICES APPLICATION**

DOCTORAL THESIS

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**SINTEZA, OPTIMIZACIJA I KARAKTERIZACIJA
GRAFENA IZ BIOMASE I NJEGOVIH
NANOKOMPOZITA ZA PRIMJENU U
ELEKTROKEMIJSKIM UREĐAJIMA ZA POHRANU
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ABSTRACT

This dissertation set out to explore whether biomass could be pushed, shaped, and refined into graphene-based materials capable of meaningful electrochemical performance. The work did not follow a single straight path, and the results did not converge toward one universal “best” material. Instead, the study uncovered how different synthesis choices pull the carbon in different directions, and how those directions matter for real applications. The first major contribution of this research is the establishment of a complete, experimentally validated route for producing graphene-like carbon from hazelnut shells. The optimized pyrolysis pathway, established through careful comparison and statistical tuning, demonstrated that biomass can be converted into partially graphitic, hierarchically porous carbon using accessible catalysts and activation agents. More importantly, it showed that the most structurally ordered carbon is not necessarily the most electrochemically capable. The second contribution lies in the oxidation and reduction work. By comparing two oxidation environments and three reduction pathways, the study revealed how sensitive biographite is to chemical treatment. GO-OPT and B-GO behaved like fundamentally different materials, even though they were produced from the same precursor. Their reduction products showed that oxygen removal and structural restoration are not synchronized processes, clarifying how biomass-derived GO responds to chemical treatment and where its limitations lie. The third contribution concerns heteroatom doping. Hydrothermal doping produced the strongest structural and electrochemical improvements, with HD-GLC7 standing out as the most balanced material in the study. Thermal doping, although less impressive in performance, offered scalability, making TD-GLC3 the practical choice for downstream work because it could be produced more easily and modified more aggressively. The fourth contribution comes from the nanocomposite investigation. The composites did not improve capacitance in the tested electrolyte, but instead

provided insight into the limitations of metal-oxide systems in organic electrolytes and how electrolyte choice can ultimately dictate material design. Altogether, these findings show that biomass-derived graphene is not a single material but a landscape of possibilities. Some routes favor conductivity, others chemical activity, and others structural stability. This dissertation mapped that landscape experimentally, delivering optimized synthesis routes for graphene-like carbon and graphene oxide, identifying an effective doping strategy, and clarifying the limits of the chosen nanocomposite and electrolyte system. The work does not claim universal improvement; it claims understanding. This fundamental understanding provides a framework for developing biomass-derived carbon materials beyond the specific systems investigated here. Future work can build on these findings by exploring more compatible electrolytes, pushing hydrothermal doping toward scalable formats, and integrating the optimized carbon frameworks into full device architectures.

Keywords: Biomass-derived carbon; Graphene oxide; Heteroatom doping; Nanocomposites; Electrochemical performance; Supercapacitors

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1. INTRODUCTION

1.1. Background of Study

Around the world, energy consumption continues to climb as industries expand, cities grow, and technology advances. This steady rise in demand puts pressure on the development of energy storage solutions that are not only efficient but also environmentally friendly [1, 2]. At the same time, moving to renewable sources like solar and wind is crucial for cutting greenhouse gas emissions. But because these renewables are not always available, there is a greater need for dependable, high-performing energy storage systems that can address supply fluctuations [3, 4].

To tackle these issues, electrochemical storage technologies—especially lithium-ion batteries and supercapacitors—play a key role. Lithium-ion batteries store a lot of energy for their size. Still, they can struggle with power output, lifespan, and safety. Supercapacitors, on the other hand, deliver energy quickly, last a long time, and can be charged and discharged rapidly. However, since they don't hold as much energy as batteries, their use is somewhat limited [5, 6]. This underscores the need to improve the materials used in their electrodes to boost overall performance [3, 7].

Among the materials being explored, carbon-based options such as graphene stand out for their excellent electrical conductivity, chemical stability, and very large surface area [8, 9]. Still, producing graphene through conventional methods is often costly, complicated, and environmentally burdensome, making large-scale production a challenge [10]. This has led researchers to explore the use of carbon materials derived from biomass—essentially turning agricultural waste into useful carbon structures that align with circular economy principles [11].

Hazelnut shells, for example, are a promising type of biomass because they contain a lot of carbon and have a lignocellulosic structure. This structure facilitates the formation of graphitic domains

when the shells are heated under controlled conditions [12, 13]. Through thermal and chemical activation, these shells can be converted into conductive carbon materials exhibiting graphene-like characteristics [14, 15].

In this research, two distinct pathways for producing graphene-based materials from hazelnut shells are explored. The first involves the simultaneous use of iron-based catalysts, such as ferrocene and ferric chloride, to promote the formation of graphitic structures, followed by treatment of the product with potassium hydroxide [16, 17]. The second method uses chemical oxidation to create graphene oxide (GO), which is then reduced to get reduced graphene oxide (rGO) [18]. Alongside developing these materials, the study also focuses on fine-tuning the processing steps, experimenting with the addition of different elements (doping), and creating nanocomposites, sometimes with the support of statistical design techniques. Adding metal oxide particles and silicon dioxide is also being tested to determine whether they boost conductivity and electrochemical performance [19].

1.2. Problem Statement

As the world rapidly moves toward electrification and renewable energy, there is growing pressure to develop energy storage materials that are not only efficient but also environmentally friendly [1]. Supercapacitors stand out here for their ability to charge and discharge quickly, deliver high power, and work reliably for many cycles. Yet their low energy density still holds them back, and making progress on this front largely depends on developing better electrode materials [20]. Graphene-based materials are often highlighted for their ability to combine high conductivity, large surface area, and robust mechanical strength, making them promising candidates for next-generation supercapacitor electrodes [8]. But producing graphene the traditional way is usually expensive, energy-intensive, and not easily scalable, which limits its practical use [10]. Using

biomass-derived graphene is a greener and more affordable option, but significant challenges remain in achieving the desired structure and consistent electrochemical performance [21].

Although iron-based catalysts are known to promote graphitization [16, 22], much remains unknown about how organometallic catalysts such as ferrocene behave in biomass systems [23]. Similarly, the process of making graphene oxide (GO) and reduced graphene oxide (rGO) through chemical oxidation and reduction looks promising, but how oxidation methods, doping with other elements, and the resulting electrochemical properties are connected remains underexplored in detail [18, 19].

There's also limited research on graphene nanocomposites derived from biomass. Most studies focus on individual steps rather than a more holistic, optimization-centered approach that connects how synthesis is carried out to changes in structure and final electrochemical performance [24, 25]. Because of this, we don't fully understand how choices like which catalyst to use, how to activate the material, doping, or making composites all work together to impact performance.

This research aims to fill those gaps with a step-by-step strategy that brings together sustainable synthesis, careful material modification, and smart engineering of nanocomposites. By fine-tuning key factors—such as which catalysts to use and in what amounts, how to activate the material, and the best ways to dope it—the study aims to establish clear links among processing, structure, and material performance [17, 26]. The ultimate goal is to move closer to scalable, high-performance graphene materials derived from biomass for use in next-generation energy storage devices.

1.3. Aim and Objectives

Aim:

This research aims to develop and improve graphene-based materials derived from hazelnut shell biomass, as well as related nanocomposites, to enhance electrochemical performance for energy storage. This study emphasizes sustainable methods for producing these materials, step-by-step process improvements, and targeted modifications. While both supercapacitors and batteries are considered, supercapacitors are the main focus because they work especially well with porous carbon materials and need to deliver high power.

Objectives:

To achieve this aim, the study pursues the following specific objectives:

1. **Make graphene** from hazelnut shells by pyrolysis and catalytic graphitization, using iron-based catalysts such as ferrocene and ferric chloride.
2. **Fine-tune important synthesis factors**—including temperature, catalyst type and amount, particle size, and activating agent—to improve how the materials are structured, their porosity, and their electrochemical performance.
3. **Create graphene oxide (GO) and reduced graphene oxide (rGO)** through carefully controlled chemical oxidation of graphitized biochar, followed by reduction using different techniques.
4. **Add heteroatom doping** (using nitrogen and sulfur) and surface functionalization to boost conductivity, capacitance, and how the materials react chemically.

5. **Make graphene-based nanocomposites** by combining modified graphene with metal oxides and other additives, and optimize their composition and structure to improve charge storage.
6. **Analyze the structural, morphological, and electrochemical properties** using advanced analytical methods to establish clear relationships between structure and properties.
7. **Test the electrochemical performance** of all the synthesized materials and composites in supercapacitor setups, and selectively test them in batteries to see how widely they can be used.
8. **Find links between synthesis, structure, and performance** to help design better, sustainable graphene-based materials for future energy storage devices.

1.4. Research Hypothesis

By systematically optimizing how these materials are produced, oxidized, and modified, it's possible to engineer biomass-derived graphene and its nanocomposites to exhibit improved structure, larger surface area, well-defined pores, and enhanced electrical conductivity. These improvements should lead to better electrochemical performance in supercapacitors and possibly make them suitable for battery use as well.

1.5. Research Questions

To accomplish the main goal of this research, these questions are explored:

1. **How do the choices made during synthesis**—like pyrolysis temperature, the type of catalyst (ferrocene vs. ferric chloride), how much catalyst is used, and the activating agent

(such as KOH or ZnCl₂)—change the structure, shape, and electrochemical properties of graphene made from hazelnut shells?

2. **What happens to the material's** shape, surface groups, and electrical conductivity during the chemical oxidation and later reduction of graphitized biochar to make graphene oxide (GO) and reduced graphene oxide (rGO)?
3. **How do methods** like adding nitrogen or sulfur (heteroatom doping) and changing the surface improve the electrochemical performance of graphene made from biomass?
4. **Which composition of** these graphene-based nanocomposites gives the best charge storage, quick charge/discharge, and stability during use in supercapacitors?
5. **How well do these materials work in real devices?** What can be learned from their supercapacitor performance to help design better energy storage devices in the future?

1.6. Significance of the Study

As the world shifts toward renewable energy and electrification, there's a greater need for energy storage materials that are both effective and environmentally friendly [1]. Supercapacitors offer great benefits—high power, fast charging and discharging, and long life—but their lower energy density still limits their widespread use [5]. That's why improving the materials used for electrodes is so important.

This research contributes by converting hazelnut shell biomass—a plentiful agricultural by-product—into graphene-based materials using two main methods: catalytic graphitization with chemical activation and chemical oxidation followed by reduction to produce graphene oxide (GO) and reduced graphene oxide (rGO). This aligns well with circular economy principles by

transforming waste into useful materials [21, 27] and offers a greener, potentially scalable alternative to traditional graphene production, which is often energy- and resource-intensive.

What makes this work unique is the use of ferrocene as a catalyst during pyrolysis to promote the formation of graphene structures. While ferrocene has been studied in other carbon systems, its behavior in lignocellulosic biomass, such as hazelnut shells, remains poorly understood [28]. Using ferrocene, along with careful activation, provides new insights into how graphitic domains form, how porosity develops, and how these factors affect electrochemical properties. The study also focuses on systematically optimizing synthesis steps, exploring different doping methods with other elements, and designing nanocomposites. By clearly linking processing steps, structure, and performance, the research deepens understanding of how to achieve optimal performance from biomass-derived graphene [25, 26]. Adding metal oxide and heteroatoms further improves charge storage, speed, and stability, especially in supercapacitors [19, 26, 29].

Overall, the significance of this study is twofold:

- **Scientific significance:** It furthers understanding of biomass-to-graphene conversion, catalytic graphitization mechanisms, and structure–property–performance relationships in carbon-based energy storage materials.
- **Practical significance:** It establishes a pathway for producing sustainable electrode materials suitable for next-generation supercapacitors, with potential relevance to selected battery systems as well.

1.7. Scope of the Study

This study examines the synthesis, optimization, and characterization of graphene-based materials derived from hazelnut shell biomass for electrochemical energy storage applications, with

particular emphasis on supercapacitors. The work spans various interrelated stages, beginning with precursor preparation and extending through material synthesis, modification, composite formation, and electrochemical evaluation.

The scope of the study includes:

1. Preparation of hazelnut shell biomass as a carbon-rich precursor suitable for graphitization and chemical oxidation.
2. Synthesis of graphene-like carbon materials through catalytic graphitization and chemical activation using iron-based catalysts (ferrocene or ferric chloride) and activating agents such as KOH, ZnCl₂, or H₃PO₄. Key parameters—including temperature, catalyst loading, particle size, and activation ratio—are systematically optimized.
3. Production of graphene oxide (GO) and reduced graphene oxide (rGO) via chemical oxidation of graphitized biochar using a modified Hummers method, followed by controlled reduction and surface functionalization.
4. Heteroatom doping with nitrogen and sulfur to enhance conductivity, surface chemistry, and electrochemical behavior.
5. Fabrication of graphene-based nanocomposites incorporating metal oxides such as Fe₂O₃ and SiO₂ with optimization of composition and structure to improve charge storage characteristics.
6. Electrochemical evaluation primarily focused on supercapacitor testing using cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical

impedance spectroscopy (EIS). Limited battery testing is conducted to assess wider relevance, although the materials are expected to exhibit capacitive behavior.

Throughout the study, emphasis is placed on establishing clear links between synthesis parameters, structural modification, and electrochemical performance. The overall goal is to provide an integrated framework for engineering sustainable graphene-based materials developed for energy storage applications.

1.8. Limitations of the Study

Several limitations of this study should be acknowledged. First, the catalysts and activating agents were not applied evenly throughout all experiments. Ferrocene and ferric chloride were used in separate synthesis runs, and activating agents such as KOH, ZnCl₂, and H₃PO₄ were introduced at different stages. This successive refinement improved material functionality but limits direct cross-comparison among all activation systems.

Second, the study relied exclusively on hazelnut shell biomass as the carbon precursor. While this allowed for controlled optimization, the findings may not be fully transferable to other biomass types with different compositions.

Third, access to advanced characterization techniques was limited. Laboratory constraints in Croatia meant that methods such as X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) were not always available. Consequently, some samples—particularly those demanding detailed surface or structural analysis—could not be examined using these techniques.

Fourth, all synthesis and electrochemical testing were conducted at laboratory scale. Issues related to industrial scalability, long-term device integration, and actual performance fall outside the scope of this work.

Finally, natural variability in biomass is unavoidable. Hazelnut shells do not have a uniform composition, and batch-to-batch differences may affect reproducibility, as is typical of biomass-derived materials.

1.9. Organization of the Dissertation

This dissertation is organized into five chapters, structured to reflect the logical progression of the research from conceptual development to experimental execution and final analysis. Each chapter addresses a distinct stage of the study, collectively yielding a coherent framework aiding understanding of the synthesis, optimization, and application of biomass-derived graphene and its nanocomposites.

2.0. LITERATURE REVIEWS

2.1. Introduction to the Chapter

This chapter surveys major developments and continuing difficulties in the field of biomass-derived graphene-based materials for energy storage, with a focus on supercapacitors. Recent progress is highlighted, but enduring obstacles and knowledge gaps — those that still shape the direction of the field — are also examined. The choice of a dual synthesis strategy is then justified, situating the work within greater efforts toward sustainable material innovation.

Two distinct synthesis routes are being considered here: (i) catalytic graphitization coupled with chemical activation to produce graphene-like carbon (GLC), and (ii) an eco-friendly oxidation process to convert biographite into graphene oxide (GO). This framework makes it possible to compare different classes of graphene-derived carbon structures directly.

As Figure 1 shows, these parallel synthesis approaches permit a structured comparison between conductive, high-surface-area carbons (GLC) and oxygen-functionalized graphene materials (GO/rGO). In addition, this dual strategy also lays the platform for future studies involving heteroatom doping and the design of advanced nanocomposites.

To provide needed context, the growing demand for sustainable, high-performance energy storage devices is first reviewed — particularly supercapacitors, which are valued for rapid charge/discharge cycles, high power output, and consistent reliability. Graphene, known for its exceptional conductivity, large surface area, and mechanical toughness, has emerged as a promising candidate for electrode fabrication. However, existing production techniques — including chemical vapor deposition, mechanical exfoliation, and chemical reduction of graphene

oxide — face major limitations. Some of these challenges include high cost, poor scalability, and considerable environmental impact, as widely noted in the literature.

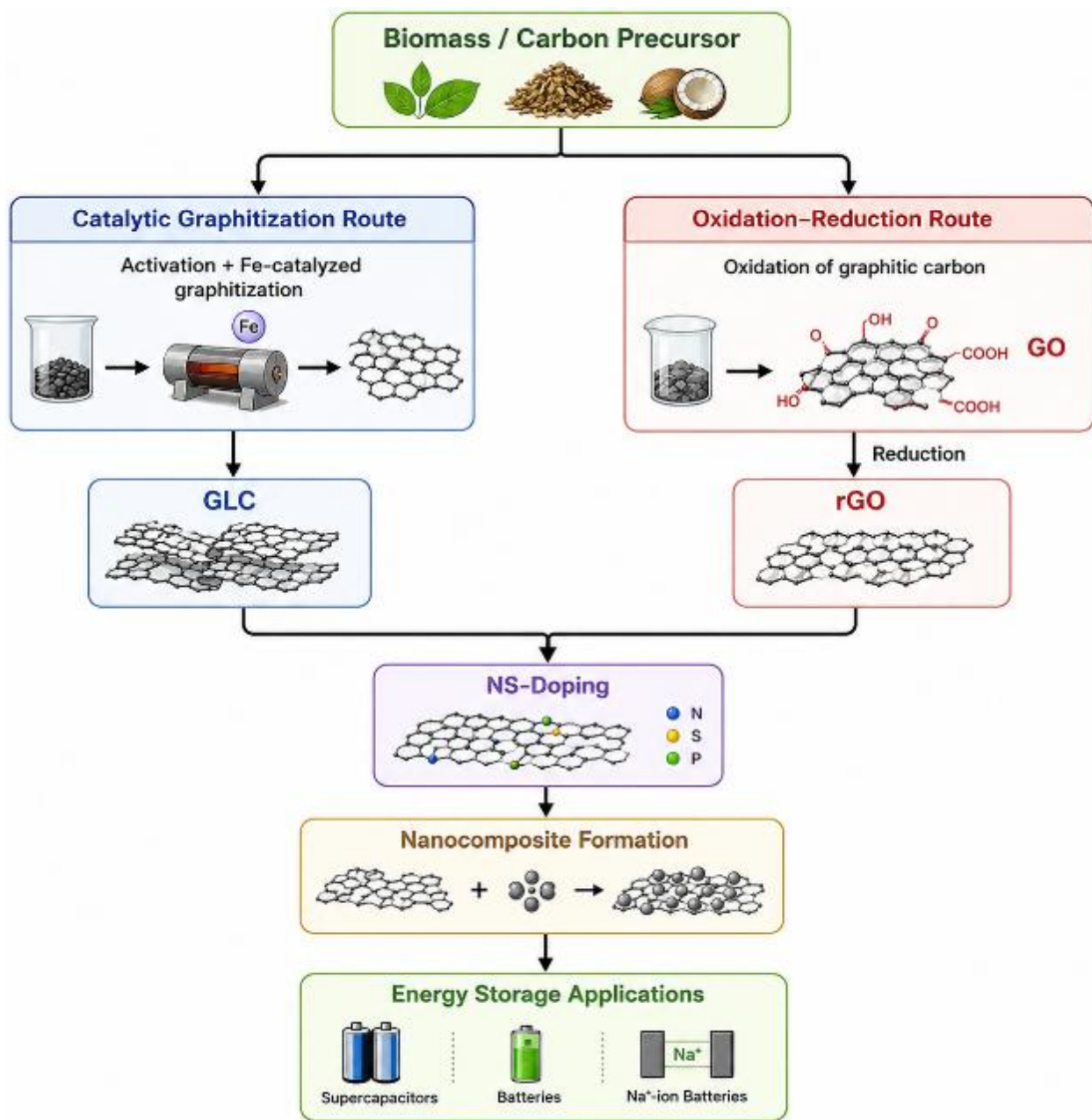


Figure 1. Schematic overview of the dual synthesis strategy. Parallel pathways for catalytic graphitization → GLC and oxidation → GO/rGO, followed by doping and nanocomposite formation.

Biomass — specifically hazelnut shells — is considered here as a renewable carbon source. The high fixed carbon content and lignocellulosic structure of hazelnut shells make them suitable for graphitization and activation. The discussion then moves to catalytic graphitization, focusing on ferrocene as a catalyst and the limitations that come with potassium hydroxide (KOH) activation. To overcome these limitations and better control the pore structure of organic electrolytes, a dual-activation strategy using phosphoric acid (H_3PO_4) and zinc chloride (ZnCl_2) is introduced.

The complementary GO synthesis pathway is also covered. This includes oxidation methods that avoid NaNO_3 , as well as the need to reduce GO—done to restore conductivity and boost electrochemical performance. Because both pathways involve many variables, the Taguchi method is presented as a systematic approach to pin down optimal synthesis conditions.

Later sections address heteroatom doping—specifically, nitrogen and sulfur incorporation via thiourea—and the formation of nanocomposites with metal oxides such as Fe_2O_3 and SiO_2 . These are meant to improve capacitance and charge transport. The chapter finishes with an overview of the characterization techniques and electrochemical evaluation methods used in the experimental work that follows.

2.2 Biomass Derived Carbons

2.2.1 Rationale for Biomass Carbon

Biomass is a renewable, abundant, and carbon-rich natural resource. This makes it a useful feedstock for functional carbon materials. Its internal structure, consisting mainly of cellulose, hemicellulose, and lignin, functions as a natural template. That template supports carbonization, porosity development, and even partial graphitization during heat treatment [26, 30, 31].

Hazelnut shells have drawn attention in the literature compared to other agrowaste materials. That comes down to three things: high fixed carbon, a dense lignocellulosic framework, and low ash content [32]. Those features support stable carbon networks and prevent inorganic impurities from disrupting activation or catalytic graphitization [33, 34]. To put this choice in context, Table 1 compares hazelnut shells with other common precursors—rice husks, almond shells, and coconut shells. Key parameters like fixed carbon, volatile matter, ash content, and lignin fraction are included. What stands out from such comparisons is that, even though many biomass sources can work, their initial composition strongly shapes the final carbon material's properties [12].

Table 1. Comparative compositional characteristics of selected biomass precursors commonly used for carbon material synthesis

Biomass precursor	Fixed carbon (%)	Volatile matter (%)	Ash content (%)	Lignin content (%)	Remarks for carbon synthesis	Source
Hazelnut shell	18–28	65–75	1–3	35–45	High lignin and low ash favor graphitic carbon formation and structural stability	[35]
Rice husk	15–20	55–65	15–25	20–30	High silica/ash content may limit graphitization but promotes thermal stability	[36]
Almond shell	20–30	65–75	1–3	30–40	Good carbon yield and relatively low ash content	[37]
Coconut shell	25–35	60–70	0.5–2	40–50	High fixed carbon and lignin support development of dense porous carbons	[38]

Biomass-derived carbons also fit with circular economy principles by turning agricultural waste into useful materials [39]. That said, they often come with structural heterogeneity and limited graphitic ordering. So extra steps — like activation and catalytic graphitization — are usually needed to boost conductivity, surface area, and pore accessibility [3, 13].

2.2.2 Thermochemical Conversion Methods

Thermochemical conversion is the main route for turning biomass into carbon-rich materials suitable for energy storage. The two commonly used thermochemical approaches are pyrolysis and hydrothermal carbonization (HTC). Each of these approaches gives different structural outcomes.

Pyrolysis

Pyrolysis means heating biomass under an inert atmosphere, typically between 400–1000 °C [11]. The process involves dehydration, devolatilization, and carbonization, ultimately producing char with higher aromaticity and carbon content [12, 40]. At temperatures above roughly 800–900 °C, some partial graphitization can occur, though significant ordering usually requires a catalyst [16, 17]. Key factors that affect pyrolysis include temperature, heating rate, residence time, and the choice of inert gas [11, 41]. When paired with catalytic graphitization or chemical activation, pyrolysis is an effective method for producing graphene-like carbon (GLC) — which is exactly what's explored in this study [16, 42].

Hydrothermal Carbonization (HTC)

HTC is performed in water at 180–250 °C under autogenous pressure [10, 43]. One advantage: it doesn't require drying the biomass beforehand. The product is hydrochar, which tends to have higher oxygen content, less graphitic ordering, and often a spherical shape [43, 44]. HTC is energy-efficient and works well for wet feedstocks [10], but the resulting materials usually require post-treatment — such as activation or high-temperature annealing — to perform well in electrochemical applications [42, 44].

Structural Evolution During Conversion

How cellulose, hemicellulose, and lignin break down during processing determines how the biomass structure evolves [12].

- **Cellulose** helps create pores as volatiles are released.
- **Hemicellulose** breaks down at lower temperatures, which influences early-stage porosity.
- **Lignin** has an aromatic structure and decomposes over a wide temperature range — it plays a central role in building stable carbon frameworks.

The way these components interact shapes the final morphology, pore structure, and degree of ordering. But without further modification, biomass-derived carbons tend to have limited conductivity and insufficient surface area for demanding energy storage applications [41].

Limitations and Need for Further Modification

So, thermochemical conversion provides a viable route to carbon materials. Still, some limitations remain:

- low graphitic ordering
- limited electrical conductivity
- suboptimal pore size distribution for electrolyte transport

Bottom line: biomass-derived carbon is the starting material in this study. Its structural quality, porosity, and degree of graphitization all strongly affect how well it can be chemically modified and how it performs for electrochemical energy storage. That is why activation strategies and

catalytic graphitization are essential — they tailor biomass-derived carbons for advanced applications like supercapacitors.

2.3. Activation Techniques

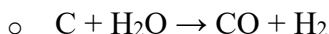
2.3.1 Physical vs Chemical Activation

Activation is a key step for making carbon materials with high surface area, tailored pore structures, and accessible electrochemical interfaces. These properties are crucial for applications such as supercapacitors, where charge storage depends heavily on the interaction between the electrode surface and the electrolyte. Activation methods generally fall into two categories: physical activation and chemical activation. Each works differently and gives different results [15].

2.3.1 Physical Activation

Physical activation works by gasifying carbonized biomass with oxidizing gases, steam or CO₂, for instance, at temperatures usually between 700–1000 °C [15]. The process typically happens in two stages:

1. The biomass is carbonized to form char.
2. The char is activated through reactions such as:



These reactions strip away carbon atoms and create porosity, mostly micropores. Physical activation is simple, uses no chemical reagents, and has a relatively low environmental footprint. On the downside, it often yields a lower surface area, takes longer, and offers limited control over pore-size distribution — which can restrict ion transport in electrochemical systems.

2.3.2 Chemical Activation

Chemical activation means soaking biomass or pre-carbonized material in activating agents such as KOH, ZnCl₂, or H₃PO₄, followed by heat treatment. Unlike physical activation, this approach usually combines carbonization and activation into a single step [42].

Different agents work through different mechanisms:

- **KOH** drives redox reactions and potassium intercalation, thereby creating abundant microporosity and high surface area [42].
- **ZnCl₂** acts as a dehydrating agent, stabilizing the carbon framework and promoting the formation of porous networks with greater mesoporosity [42].
- **H₃PO₄** promotes cross-linking and prevents tar formation, yielding materials with mixed micro- and mesopores and improved surface functionality [42].

Chemical activation generally outperforms physical activation in terms of surface area, pore development, and tunability. Still, which agent you pick ends up shaping the final pore structure and electrochemical behavior in a big way [15].

2.3.3 Challenges in Chemical Activation

Even with its advantages, chemical activation comes with several practical and structural problems:

Pore Structure Control

Getting the right balance between micropores and mesopores is tricky. Too much microporosity — which is common with KOH-activated carbons — can get in the way of ion transport, especially

in organic electrolytes where solvated ions are larger. So mesopores are essential for improving diffusion and cutting down resistance [45].

Harsh Chemical Conditions

Chemical activation often uses corrosive reagents and high temperatures. That can mean equipment damage, safety issues, and environmental headaches. The post-treatment steps — such as washing to remove residual chemicals — also generate a large volume of wastewater.

Cost and Scalability

Due to the chemicals used, the labor-intensive washing process, and the handling of waste produced during chemical activation, their cost increases. Scaling up isn't only about making more; it's increasingly about making smart choices that account for a system's performance, real-world environmental sustainability, and economic viability.

2.3.4 Dual Activation Strategies

Having a low quantity is not sufficient at times to get the desired fine, complex pore structure. KOH works well for micropores, but it mostly guides the material in that direction. When activating agents are paired, each has a slightly different influence on the carbon. This collaboration usually allows you to control pore maturation and makes the final structure more stable.

Synergistic Roles of Combined Agents

It combines activating agents like $\text{H}_3\text{PO}_4 + \text{ZnCl}_2$ or $\text{H}_3\text{PO}_4 + \text{KOH}$ to enable an optimization of what each agent does best:

- H_3PO_4 has a structural stabilizing and cross-linking effect.

- ZnCl_2 enhances mesopore formation and pore connectivity.
- KOH generates high microporosity and an extensive surface area.

All these effects, in concert, produce carbons with hierarchically porous structures, enhanced ionic transport, and greater structural integrity during carbonization.

Relevance to Organic Electrolytes

Dual activation is especially useful in organic electrolytes, where the ions are larger and need bigger channels to move through. By striking a balance between tiny micropores for charge storage and larger mesopores for ion transport, dual activation helps ensure that ions can move freely and the material performs well in real-world conditions.

Integration with Catalytic Graphitization

Activation processes can interact with catalytic graphitization by influencing carbon rearrangement, defect formation, and the interactions between catalysts and carbon. Combining activation with catalytic graphitization enables tuning of conductivity, porosity, and surface chemistry simultaneously — which is essential for good electrochemical performance.

Summary

Dual activation strategies go beyond what conventional chemical activation can achieve by enabling finer control over pore structure and surface characteristics. By pairing activating agents with complementary mechanisms, biomass-derived carbons can be produced with better accessibility, conductivity, and structural stability — all of which matter for advanced energy storage applications. These structural and textural improvements provide a solid foundation for subsequent surface functionalization. When combined with compositional modification,

particularly via heteroatom doping and composite formation, this further enhances electrochemical performance.

2.4 Catalytic Graphitization

2.4.1 Iron-Based Catalysts

Activation strategies mostly tune porosity and surface chemistry. Catalytic graphitization does something different — it improves structural ordering and aids in the formation of graphitic domains [16, 46].

Among the catalysts available, iron-based ones receive the most attention. They are active, available, and fairly cheap [46]. Common examples include ferrocene, ferric chloride (FeCl_3), and metallic iron (including nano iron). How these catalysts behave chemically — and how they break down — affects their interactions with carbon precursors. That in turn, determines the quality of the graphitic structures [16].

- **Ferrocene** breaks down at high temperatures into evenly distributed iron nanoparticles. Those nanoparticles act as well-dispersed catalytic sites, which leads to more homogeneous graphitic domains.
- **Ferric chloride (FeCl_3)** is usually added via solution impregnation. When heated, it gets reduced to iron or iron oxide species, which then catalyze carbon rearrangement. It is cheap and easy to work with. One limitation is that it does not always disperse as evenly in biomass matrices as ferrocene does.

- **Metallic iron** — especially at the nanoscale — gives an active catalytic phase without needing decomposition. Its high surface area helps carbon-metal interactions. But particles can clump together, and that hurts reproducibility.

How Iron Catalyzes Graphitization

Iron-driven graphitization mostly follows a dissolution-precipitation mechanism [46, 47]:

1. Active iron species form.
2. Carbon is incorporated into the metal catalyst.
3. Carbon is transported through/along the catalyst.
4. Carbon precipitates as graphitic carbon once the catalyst becomes sufficiently carbon-rich.

Some studies also point to a carbide-mediated pathway involving Fe_3C [16]. Either way, how well graphitization works depends on temperature (typically 700–1000°C), catalyst loading, particle size, and the interaction between the catalyst and carbon precursor.

2.4.2 Past Applications and Limitations

Iron-based catalysts have been used a lot on synthetic carbon precursors — polymers, phenolic resins, pitch, that sort of thing. Those precursors have uniform compositions, so catalyst dispersion is easier to control and graphitic ordering stays consistent [46, 48]. Ferrocene, FeCl_3 , and nano iron have all been used to produce carbons with improved conductivity and crystallinity in those systems — using pulverized biomass as the starting carbon precursor.

But applying the same approach to biomass-derived carbons is a much bigger challenge — and one that is still not fully solved. Biomass as a carbon source is fundamentally more complex, and that human element is part of what makes this field meaningful. Each type of biomass brings its

own unique story, shaped by environmental conditions, growth cycles, and even local ecosystems. This diversity means researchers are not just dealing with chemistry, but with the unpredictability and richness of nature itself. As a result, several complications arise:

- heterogeneous composition.
- variable lignocellulosic structure
- inorganic impurities
- non-uniform decomposition behavior

Ultimately, making progress in this area is not just about solving technical problems — it is about embracing the variability of natural materials and developing strategies that can adapt to it. This human-centered approach could make the resulting carbons not only more sustainable but also more broadly relevant to real-world applications.

All of that can mess with catalyst dispersion, change reaction pathways, and lower graphitization efficiency [49]. Specific problems reported in the literature include:

- uneven catalyst distribution inside biomass matrices
- leftover metal particles that need post-treatment
- trade-offs between graphitic ordering and porosity, especially when activation is also in play

Still, despite these headaches, more recent studies are showing interest in combining catalytic graphitization with biomass conversion, increasing the potential to produce graphene-like carbons from renewable sources [16].

2.4.3 Research Gap and Relevance

Iron-catalyzed graphitization works well for synthetic precursors. But how it behaves in biomass-derived systems remains poorly understood [49]. Specifically, no readily accessible research is available on how biomass composition, chemical activation, catalyst type, catalyst loading, and catalyst dispersion interact to influence graphitization pathways when systematically optimized using a design such as Taguchi or Box-Behnken.

Filling those gaps matters if scalable, sustainable routes to graphene-like carbons from renewable feedstocks are going to be developed.

Even when catalytic graphitization improves structural ordering, but control over surface functionality or oxygen-containing groups is not established. And those are critical for interfacial chemistry and electrochemical tailoring. That's exactly why a complementary graphene oxide-based pathway is useful — oxygen-containing functionalities, along with reduction and doping strategies, offer an alternative route for precise surface engineering.

2.5. Graphene and Graphene Oxide

In the context of this study, graphene and graphene oxide are fundamental carbon-based materials of interest for electrochemical energy storage due to their structural versatility and electrochemical tunability. They differ structurally mainly in the oxygen-containing groups attached to the graphene oxide sheets. These groups induce wrinkles and folds in the sheets, unlike pristine graphene, which has a more planar structure, as illustrated in Figure 2.

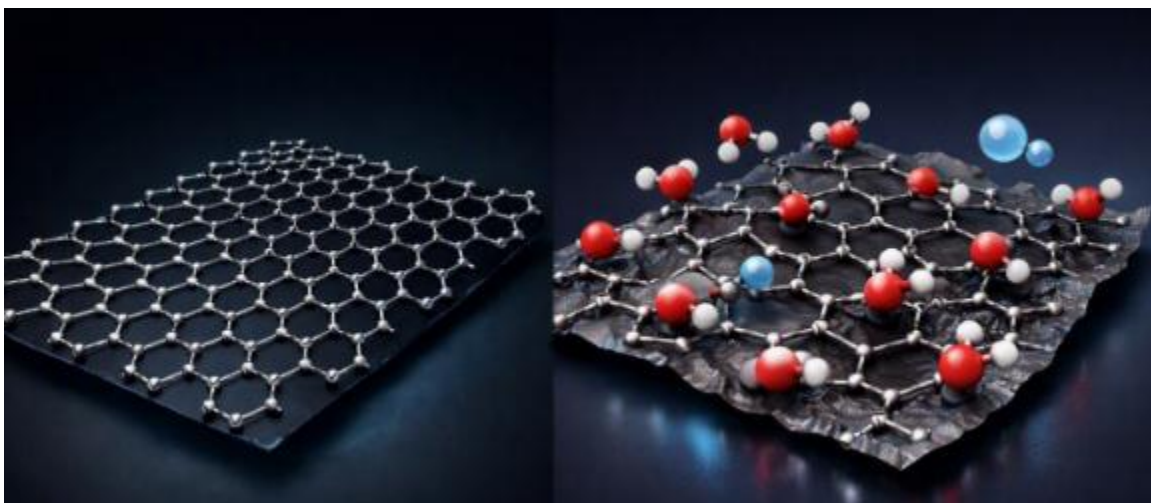


Figure 2. Atomic models showing pristine graphene and oxidized graphene oxide structures.

2.5.1. Graphene Properties and Advantages for Energy Storage

Graphene is basically a two-dimensional sheet of carbon atoms arranged in a hexagonal lattice, held together by sp^2 bonds [50]. But that simple structure gives it some remarkable properties: exceptional electrical conductivity, a theoretical surface area around $2630 \text{ m}^2/\text{g}$, and remarkable mechanical strength. These properties position graphene as a top candidate for energy storage including supercapacitors and lithium-ion batteries [51, 52].

Some of the factors that work in favor of graphene in electrochemical energy storage applications are:

- **Electron transport efficiency.** The π -conjugated network extends across the sheet, so electrons move fast along the basal plane. That means less resistive loss in the electrodes.
- **Defect density (though low, compared to other carbon materials).** Sure, structural imperfections such as vacancies or Stone–Wales defects might seem like problems. But

they actually modify the electronic behavior and create chemically active spots. Those spots can be used for functionalization or doping.

- **Lots of surface area for storing charge.** With that much accessible surface area, electric double-layer capacitance (EDLC) works well. And if you dope in some heteroatoms, you can get pseudocapacitive contributions on top of that. So, overall charge storage increases [53].

Put all that together, and graphene becomes a pretty flexible platform for designing advanced electrode materials. Table 2 backs this up — it compares surface area, electrical conductivity, and potential electrode applications across different carbon systems [4, 54-58].

Table 2: Properties and uses of carbon electrode materials.

Material	Surface Area m ² /g	Conductivity (S/cm)	Typical Use
Graphene	2630 (theoretical)	10 ⁴	Supercapacitor electrode
Graphite	10–20	10 ³	Battery Anode
CNTs	200–400	10 ² –10 ³	Hybrid electrodes
Activated Carbon	500–2500	1–10	EDLC supercapacitor

2.5.2. Graphene Oxide (GO) Synthesis and Reduction Methods

Graphene oxide is an oxygen-rich derivative of graphene. Its high density of functional groups, hydrophilicity, and tunable electronic properties make it a versatile precursor for carbon-based materials [18].

The synthesis of graphene using this method proceeds in two stages. The first stage involves oxidizing a graphitic precursor to introduce oxygen-containing functional groups. This expands the interlayer spacing. Then, reduction partially restores the sp^2 carbon network. The oxidation and reduction routes used in graphene synthesis via chemical oxidation shape the structural disorder, functional group distribution, and electrochemical behavior of the produced graphene [18].

2.5.2.1 Oxidation Methods

Conventional Hummers Method

The Hummers method [59] remains widely used. In this method, $KMnO_4$ serves as the primary oxidant in concentrated H_2SO_4 , while $NaNO_3$ promotes intercalation. The oxidation of the graphite introduces epoxy, hydroxyl, and carboxyl groups across the graphite lattice. This results in the expansion of the interlayer spacing and disrupts the π -conjugated network. This method is reliable and produces strongly oxidized GO. But there are drawbacks. $NaNO_3$ generates NO_2/N_2O_4 gases — an environmental and safety concern. Extensive washing is needed to remove residual ions [60]. Additionally, the harsh conditions can introduce excessive defects [61].

$NaNO_3$ -Free (Tour) Method

Methods are being explored to eliminate the use of $NaNO_3$. One such method is the improved Hummer method, also known as the Tour method. Tour modification eliminates $NaNO_3$. More sulfuric acid is used; likewise, more $KMnO_4$ is used, with H_3PO_4 introduced into the GO synthesis, creating a mixed H_2SO_4/H_3PO_4 system [62]. This mixture enhances intercalation and moderates the oxidation environment. The resulting GO often has a more uniform distribution of oxygen functionalities [63]. Removing nitrate from the oxidation process prevents toxic NO_x emissions,

improving safety and environmental compatibility. As a trade-off, the reaction typically proceeds more slowly. And phosphate residues may persist if not thoroughly washed out.

Boric Acid–Modified Hummers Method

More recent variations explore incorporating boric acid (H_3BO_3) to tune the oxidation environment [64]. In this pathway, boric acid interacts with hydroxyl groups during oxidation. This interaction influences defect formation and promotes greater interlayer expansion. As a result, the method has the potential to produce GO with modified defect distributions and enhanced spacing, which can benefit ion transport.

However, the method is not yet well standardized. Residual boron species may require additional purification.

2.5.2.2 Reduction Methods

After oxidation, GO is typically reduced to restore electrical conductivity. This is done by partially re-establishing the sp^2 carbon network. The choice of reduction method strongly influences defect density, conductivity, and electrochemical behavior.

Chemical Reduction

Chemical reduction uses electron-donating species to remove oxygen-containing functional groups.

- **Hydrazine hydrate (N_2H_4)** is highly effective but is also toxic [65, 66].

- **Ascorbic acid** ($\text{C}_6\text{H}_8\text{O}_6$) provides a greener alternative with lower toxicity [52, 67].
- **Sodium borohydride** (NaBH_4) is a strong reducing agent but can introduce boron-based impurities [68].

Chemical reduction can be carried out at low temperatures and can enhance conductivity. However, residual reagents may be difficult to remove, and the degree of reduction achieved is often lower than with thermal methods. One advantage over thermal methods is that it improves wettability when used to fabricate electrodes for electrochemical energy storage devices.

Thermal Reduction

Thermal reduction requires heating the GO to 400–800 °C under an inert or reducing atmosphere. High temperatures drive off oxygen groups as gaseous species. This high-temperature process restores the conjugated network. One of its advantages is that it avoids chemical residues and typically produces higher conductivity. However, rapid oxygen removal can cause sheet restacking or partial structural collapse, which may reduce accessible surface area [69, 70]. It can also result in porous rGO due to the evolution of gaseous species.

Hydrothermal Reduction

Hydrothermal reduction is carried out in sealed autoclaves at 150–250 °C [71]. Heat and pressure promote the self-reduction of GO. The process often restructures GO into three-dimensional hydrogel-like networks with interconnected porosity. This can enhance ion transport [72]. The degree of reduction is less controllable, and high-pressure equipment increases cost and safety requirements.

Electrochemical Reduction

Electrochemical reduction applies controlled potentials to GO films on conductive substrates [73]. Electron transfer selectively removes oxygen groups, allowing fine control over the degree of reduction. This is one of the reduction methods that yields low-defect rGO. Electrochemical reduction operates at room temperature and avoids the use of chemical reagents, making it suitable for device-integrated films. The main limitation is that it is effective only for thin films, not bulk powders [74].

Plasma Reduction

Plasma-based reduction, which is less common than others, uses argon or hydrogen plasma to remove oxygen groups [75]. Energetic plasma species enable rapid, surface-selective deoxygenation while introducing controlled defect sites. Two of the advantages of this method are that it does not require elevated temperatures and enables precise surface modification. However, the penetration depth is limited, and the equipment is specialized and costly [76].

Table 3 summarizes these reduction methods for comparison.

Table 3: Comparative Overview of GO Reduction Methods

Reduction Method	Conductivity Achieved	Structural Impact	Scalability	Typical Uses
Chemical (Hydrazine)	High	Moderate defect	High	Lab and industrial applications
Chemical (Ascorbic)	Medium	Mild defect	Medium	Green synthesis
Thermal	Very high	Potential restacking	Very high	Highly conductive rGO
Hydrothermal	Medium	Porous 3D structures	Low	Electrodes
Electrochemical	Medium	Surface only	Low	Thin films
Plasma	Medium–high	Surface defects	Low	Surface treatment

2.5.2.3. Implications for Electrochemical Performance

The selected reduction method significantly affects a few key things:

- **Electrical conductivity** — this one is critical for charge transport
- **Defect density** — influences double-layer formation and pseudocapacitance.
- **Layer spacing and restacking** — changes how easily ions can get in.

For supercapacitors specifically:

- **Thermal reduction** tends to give the highest conductivity.
- **Hydrothermal methods** generate porous networks with surfaces that ions can actually reach.
- **Chemical reduction with ascorbic acid** offers a trade-off: greener, but still decent conductivity.

The reduction method chosen for graphene oxide significantly shapes the structural, surface, and electrochemical properties of the resulting reduced graphene oxide [77]. Some studies have compared single-step versus multistep strategies. Multistep approaches — such as chemical reduction followed by thermal treatment — can yield rGO with improved structural features such as higher carbon content, and more tailored pore architecture [70]. These structural differences then translate into distinct capacitance and ion-transport behavior when rGO is used as a supercapacitor electrode. So the choice of reduction strategy matters [70].

But controlling oxygen content and restoring the structure through reduction can only partially achieve the desired properties. Further tuning can be done by deliberately modifying the carbon lattice at the atomic level. That is where heteroatom doping comes in — a complementary strategy for engineering the electronic structure and surface chemistry of graphene-based materials.

2.6 Heteroatom Doping

Heteroatom doping means intentionally sticking non-carbon atoms into carbon lattices. It's a powerful way to tailor the electronic, chemical, and electrochemical properties of graphene-based materials. For energy storage carbons, doping with heteroatoms like nitrogen (N) and sulfur (S) can change the local electronic structure, introduce sites where charge can be stored, improve how well water wets the surface, and add pseudocapacitive behavior on top of the usual electric double layer capacitance [78, 79].

2.6.1 Nitrogen and Sulfur Doping

Fundamental Concepts

Nitrogen and sulfur are the two most studied heteroatoms for doping graphene. The reason is that they modify the electronic structure while remaining chemically compatible with carbon frameworks [78, 79].

Nitrogen has about the same atomic radius as carbon but a higher electronegativity, which affects the electron distribution in the π -conjugated network and can shift the Fermi level. Sulfur has a larger atomic size, but its electronegativity is close to that of carbon. So it can disrupt the carbon lattice while introducing defect sites that boost charge storage capacity [78].

Nitrogen doping can happen in several configurations — pyridinic, pyrrolic, graphitic (also called quaternary), and oxidized nitrogen. Each configuration affects electronic properties and electrochemical activity differently. Pyridinic and pyrrolic N sites are often linked to better pseudocapacitive contributions because they can participate in Faradaic reactions. Quaternary N, on the other hand, mainly enhances electrical conductivity [78, 80].

Sulfur atoms typically show up in the carbon lattice as thiophene-like, sulfide, or sulfoxide functional groups. These sites can create localized electronic states that help with rapid charge transfer and increase surface wettability. Both benefits help electrochemical performance [79].

Doping Precursors and Mechanisms

Thiourea (NH_2CSNH_2) is one of the most common precursors for simultaneous nitrogen and sulfur doping. Under the right thermal or hydrothermal conditions, thiourea breaks down into reactive N- and S-containing species. These species then substitute into the carbon matrix during high-temperature treatment [78, 79].

Depending on the synthesis route, doping can happen in a couple of ways:

- **Hydrothermal Doping:** The carbon material (graphene, biochar, etc.) is treated with thiourea in a sealed autoclave at elevated temperatures — typically 150–250 °C. The aqueous environment and moderate pressure facilitate the incorporation of dopant atoms into defect sites. This often produces a porous structure with more active sites [81].
- **Thermal Doping:** Here, the carbon material and dopant precursor are heated together under an inert atmosphere. Higher temperatures, typically 700–900 °C. The thermal energy drives substitutional doping — N and S atoms replace carbon atoms in the lattice or bind at defect or edge sites [80, 82].

Both methods produce a range of dopant configurations. Temperature, precursor ratio, and reaction environment all influence the outcome. The relative amounts of different nitrogen configurations (pyridinic vs graphitic) and sulfur species (thiophene-like vs sulfide-like) will determine the electronic and electrochemical characteristics of the doped carbon [78, 79]. Figure 3 gives a schematic illustration of a carbon material being doped with both nitrogen and sulfur atoms.

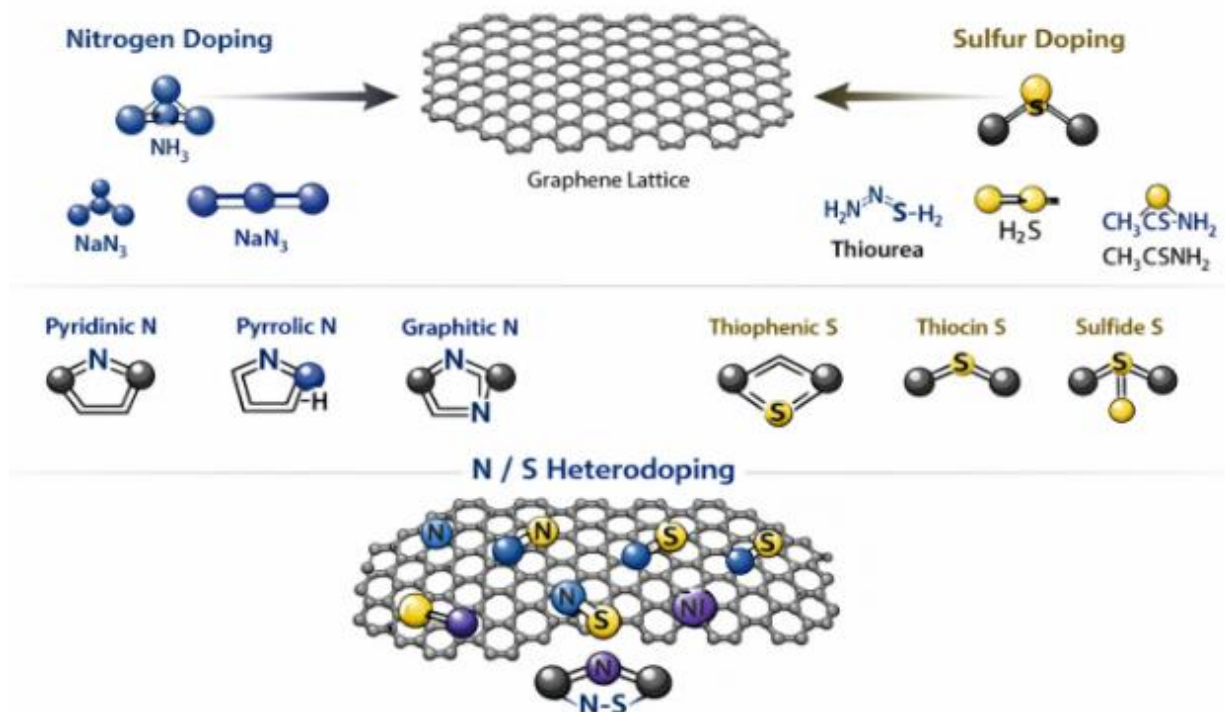


Figure 3. Schematic representation of nitrogen and sulfur incorporation into the graphene lattice, showing typical bonding configurations (pyridinic N, pyrrolic N, thiophene-like S, etc.).

2.6.2 Impact on Electrochemical Performance

Heteroatom doping influences electrochemical performance through several mechanisms, some of which are:

1. Electronic Structure and Conductivity

Doping with nitrogen and sulfur changes the electronic density of states in carbon materials. The result is often lower charge transfer resistance. Electrical conductivity is also improved.

Graphitic N deserves special mention. It donates electrons and enhances conductivity. Pyridinic and pyrrolic N sites work differently. They localize charge and help Faradaic processes along [78].

Sulfur doping works a bit differently. It introduces new states near the Fermi level and increases polarizability. This allows stronger ionic interactions and better charge transfer within the electrode. The different electronegativities of carbon and dopant atoms lead to a localized charge distribution. This can foster additional pseudocapacitive reactions [79].

1. Pseudocapacitance and Active Sites

Double-layer capacitance is physical. Heteroatom sites enable reversible redox reactions at specific potentials. Pyridinic N, for instance can introduce redox-active sites. These can store charge through Faradaic contributions. Such reactions supplement the usual electric double-layer storage. The result is a significantly higher specific capacitance than undoped carbon [78]. Sulfur heteroatoms can probably introduce active centers for pseudo-electrochemical processes. When nitrogen and sulfur are co-doped, synergistic effects can appear. Electrons transfer more easily across defect networks. Increased surface wettability improves electrolyte access to the active sites [80].

2. Surface Wettability and Ion Accessibility

Heteroatom doping can increase surface polarity and enhance interaction with electrolyte ions. The relevance is that improved wettability allows ions to penetrate more deeply into the porous network. Diffusion resistance goes down. Rate capability goes up. This improved accessibility is especially important for organic electrolytes. Without it, ion size and solvation shell effects greatly limit performance in microporous carbons [83].

Comparative Studies and Performance Trends

Studies comparing undoped and doped carbon materials consistently show that doping improves performance.

For instance, nitrogen-doped graphene shows higher capacitance and better cycle stability than pristine graphene. The reasons are enhanced surface wettability and more active sites [81, 84].

Table 4 summarizes several studies on how doping affects the electrochemical performance of various carbon materials — especially graphene-based materials — when used as supercapacitor electrodes.

Table 4. Literature summary of doping methods (hydrothermal vs thermal), dopant ratios or concentrations, and the corresponding improvements in specific capacitance or other electrochemical metrics for N- and S-doped graphene and related carbon materials.

Study	Doping Method	Dopants (N, S)	Dopant Levels	Electrolyte	Capacitance	Note
[78]	Thermal	N	4 at.% N	Aqueous	250 F g ⁻¹	Graphitic N improved conductivity
[80]	Hydrothermal	N, S	8.04 wt.% N 1.95 wt.% S	Aqueous	386.5 F g ⁻¹	High defect density; 94.5% stability
[82]	Microwave-assisted method	N, S	14.94 at.% N 4.35 at.% S	Aqueous	310 F g ⁻¹	Also displayed good performance in organic and ionic electrolytes
[84]	Hydrothermal + thermal	N, S	1.42 at.% N 1.76 at.% S	Aqueous	416 F g ⁻¹	L-cysteine solution was used as N, S source
[81]	Hydrothermal	N, S	1.50 at.% N 0.30 at.% S	Aqueous	431 F g ⁻¹	Methionine was used as dopant for the N, S-G hydrogel
[83]	Hydrothermal	N, S	- at.% N 4.10 at.% S	Ionic	180.5 F g ⁻¹	Trithiocyanuric acid was used as dopant for the NS-G aerogel
[85]	Reflux (thiourea-controlled reduction/doping)	N, S	15.19 wt.% N 26.85 wt.% S	Aqueous	465.21 F g ⁻¹	Optimized S/N ratio (1.768) enhances capacitance; excess thiourea reduces performance; 119% retention

Continuing from Table 4, co-doping with nitrogen and sulfur is a particularly effective way to improve the electrochemical properties of a material. The mechanisms are complex. They depend on the dopant ratio and configuration. But co-doped materials often combine several benefits such as improved conductivity, enhanced pseudocapacitance, and better ion accessibility. The result will be a higher specific capacitance and superior rate performance in a supercapacitor [80, 84, 85].

Challenges and Future Directions

Despite these clear advantages, heteroatom doping also comes with several challenges. For instance, excessive doping can introduce structural defects. This in turn reduces the electrical conductivity of the material, hence compromising the long-term cycle stability of the electrochemical storage device made with the doped material as electrode active material. Achieving uniform and controlled dopant distribution is also difficult. This is especially true in biomass-derived systems. The inherent heterogeneity of the precursor can influence outcomes. Optimizing dopant type, ratio, and bonding configuration for specific electrochemical applications requires systematic study. These limitations suggest that while heteroatom doping is effective for tuning the intrinsic electronic structure of carbon materials, additional performance gains often require a complementary strategy, such as one operating at a higher structural level. That brings us to the integration of graphene-based materials with secondary functional phases.

2.7 Graphene-Based Nanocomposites

A major resulting strategy focuses on nanocomposite electrodes that combine carbon materials and metal oxides. The motivation for this approach is to overcome the intrinsic limitations of each component when used alone.

Carbon-based materials such as graphene, reduced graphene oxide (rGO), and graphene-like carbon (GLC) are known for their excellent conductivity, high surface area, and stability. On the other hand, they are dominated by electric double-layer capacitance (EDLC), which limits their energy density.

Metal oxides, such as ferric oxides, are known for their substantial pseudocapacitive charge storage via reversible redox reactions, but they have poor conductivity and limited cycling stability on their own. Integrating metal oxide nanoparticles with graphene derivatives addresses these drawbacks. The resulting composites leverage the EDLC and pseudocapacitance features of both materials, yielding superior performance compared to either constituent alone [86].

These graphene-metal oxide composites are usually synthesized using methods such as hydrothermal synthesis, solution mixing, in situ growth, and solvothermal processes. These approaches enable uniform loading of metal oxide nanoparticles onto the graphene matrix. They also create strong interfacial contact. This contact is essential for efficient charge transfer [87, 88].

2.7.1 Metal Oxide Integration

Some reasons Iron oxides are widely used for supercapacitor electrodes include their relative abundance, low cost, and environmental compatibility. However, they suffer from poor conductivity and structural instability from cycling-induced volume changes. Making nanocomposites using iron oxides with graphene-based materials is effective because graphene offers conductive pathways and mechanical buffering [89, 90].

Early research revealed that when Fe_2O_3 nanoparticles are combined with graphene, the hybrid consistently performs better than either material alone. The two components deliver a complementary effect on the energy storage device, such as a supercapacitor — graphene

contributes fast EDLC behavior, while iron oxides add Faradaic redox activity. In one representative study, an Fe_2O_3 –graphene composite delivered about 226 F g^{-1} at 1 A g^{-1} in $1 \text{ M Na}_2\text{SO}_4$, outperforming pristine graphene thanks to improved charge storage and easier ion access [91].

This gain is pushed further by more sophisticated designs, such as three-dimensional Fe_2O_3 /graphene aerogels. Their interconnected porous networks allow electrolytes to move freely and charges to travel efficiently. As a result, some of these systems report specific capacitances around 440 F g^{-1} along with excellent long-term cycling stability. The advantage comes from their hierarchical architecture and the greatly increased electroactive surface area [92].

Researchers have gone beyond simple two-component systems by developing ternary composites by adding conducting polymers or other functional phases. These additions aim to boost the pseudocapacitive contribution and fine-tune mechanical properties. Their performance, however, depends strongly on the electrode configuration and the electrolyte environment [93, 94].

Put together, integrating Fe_2O_3 with graphene derivatives reliably improves capacitance and rate capability. The combination overcomes the conductivity limitations of iron oxides while preserving structural stability during repeated cycling. This is a balance that neither material can effectively achieve independently [95, 96].

A different example is silicon dioxide (SiO_2). While silica itself has limited pseudocapacitance, it can play a structural role in nanocomposites that significantly benefits electrochemical properties.

SiO_2 nanoparticles in carbon matrices prevent graphene sheets from restacking, create mesoporous structures, and improve mechanical integrity and electrolyte access [97, 98].

- Composites such as rGO/SiO₂ and other graphene-silica hybrids exhibit moderate yet stable capacitive performance. The presence of SiO₂ mainly modulates porosity and supports ion transport. It does not contribute directly to Faradaic reactions [98].
- In related systems — CoFe₂O₄/ SiO₂, for example — the synergy between ferrite and silica has yielded a specific capacitance of 316 F g⁻¹ at 0.5 A g⁻¹ with excellent cycling stability (95% retention over 5000 cycles) [99]. This shows that metal oxide-silica integration can be effective even when silica itself does not participate directly in electrochemical redox processes.

In conclusion, combining iron oxides and SiO₂ with graphene derivatives yields hierarchical composites. It will result in a system that combines conductive carbon networks, redox-active metal oxide sites, and structural modulation from silica and other components. The end result will likely be structural synergies that will enhance electrode performance across multiple dimensions.

2.7.2 Rationale for Capacitive Enhancement

The main reason for integrating metal oxides into graphene-based electrodes is straightforward: it enables simultaneous utilization of EDLC in the graphene matrix and pseudocapacitance in the metal oxides.

In a graphene/Fe₂O₃ composite, conductive graphene will facilitate fast electron transport, while the iron oxides will contribute to redox charge storage via Fe²⁺/Fe³⁺ transitions. This dual mechanism will likely increase the specific capacitance and energy density of the nanocomposite beyond those of EDLC alone [89, 91]. Also, uniformly dispersed nanoparticles provide abundant active sites. Mesoporous architectures help ion diffusion by reducing diffusion resistance. They improve the rate capability. The hierarchical pore structure in composites creates a balance

between micropores (which give high surface area) and mesopores (which support ion transport). That balance is critical for high performance in both aqueous and organic electrolytes [86, 88].

If silica is added to the matrix, it will likely enhance the structural robustness of the nanocomposite and prevent graphene sheets from restacking. That ensures the accessibility of active sites and supports mechanical stability under repeated cycling, resulting in high retention. SiO₂ contributes minimally to redox capacitance. But its role in pore structure organization and electrode integrity is significant for long-term performance [97, 98].

2.7.3 Past Studies and Performance Trends

A growing number of experimental studies back up the benefits of graphene–metal oxide composites. Some examples include:

- **Fe₂O₃/graphene composites** prepared via hydrothermal and other solution-based methods consistently exhibit significantly higher specific capacitance than either graphene or Fe₂O₃ alone. In one study, adding Fe₂O₃ produced a composite electrode that hit 226 F g⁻¹ at 1 A g⁻¹ in 1 M Na₂SO₄ electrolyte — well above what pure graphene managed [91].
- **Three-dimensional aerogel nanocomposites** consisting of Fe₂O₃ and graphene have achieved specific capacitance values of approximately 440 F g⁻¹, while also maintaining stable cycling performance over thousands of cycles. This enhanced performance is attributed to improved ion transport and increased charge accessibility within the porous network structure [92].
- Studies incorporating conducting polymers, such as polyaniline, with Fe₂O₃/graphene composites have achieved even higher specific capacitance values, exceeding 1000 F g⁻¹ in

ternary hydrogel systems. However, these values vary considerably depending on the electrolyte and device configuration employed [93].

- Metal-oxide/silica composites, including systems such as $\text{CoFe}_2\text{O}_4/\text{SiO}_2$, have demonstrated robust cycling performance, maintaining approximately 95% capacitance retention and delivering a moderate 316 F g^{-1} . Collectively, these findings indicate that silica stabilizes the redox-active phase and reinforces the overall structure, thereby preventing degradation during repeated cycling [99].

Taken together, this conveys a vital message. Metal oxide integration affects not just charge storage capacity but also rate performance and cycle stability — all key factors for real-world device applicability, as shown in Table 5. Graphene provides the conductive backbone. Metal oxides contribute redox activity. Silica or similar structural modifiers support accessibility and mechanical integrity.

Table 5. Comparison of representative graphene/metal oxide nanocomposites and electrochemical performance metrics (specific capacitance, energy density, cycle life).

Composite System	Key Electrochemical Metrics	Performance Notes	Reference
α -Fe ₂ O ₃ /rGO	970 F g ⁻¹ @ 1 A g ⁻¹ ; ~75 % retention after 2000 cycles	High specific capacitance due to dense dispersion of α -Fe ₂ O ₃ on rGO	[89]
Fe ₂ O ₃ nano-dots @ N-doped graphene	~274 F g ⁻¹ @ 1 A g ⁻¹ ; ~140 F g ⁻¹ @ 50 A g ⁻¹	Excellent rate capability from Fe ₂ O ₃ dots on conductive N-doped graphene	[90]
Fe ₂ O ₃ /graphene composite	356 F g ⁻¹ @ 1 A g ⁻¹ ; 91 % retention @ 2000 cycles	Balanced capacitance and stable cycling in aqueous electrolyte	[95]
Fe ₂ O ₃ @PPy/rGO ternary	442 F g ⁻¹ @ 1 A g ⁻¹ ; E ~61.39 Wh kg ⁻¹	Ternary design improves energy density and stability	[94]
3D Fe ₂ O ₃ @C-rGO	211 F g ⁻¹ @ 0.5 A g ⁻¹ ; 177 F g ⁻¹ @ 20 A g ⁻¹ ; stable over ~2500 cycles	Hierarchical network improves ion/electron transport	[100]
rGO/n-SiO ₂ composite	166.9 F g ⁻¹ @ 0.1 A g ⁻¹ ; 95.51 % retention after 4000 cycles; 23.2 Wh kg ⁻¹ @ 50 W kg ⁻¹	Uniform SiO ₂ dispersion on rGO improved active sites and cycling stability	[98]
rGES/PANI composite	555 F g ⁻¹ ; 91 % retention after 1500 cycles @ 0.1 A g ⁻¹	SiO ₂ integration suppressed rGO restacking and improved surface area utilization	[97]
Fe ₂ O ₃ /RGO/Fe ₃ O ₄ @Fe nanocomposite	337.5 mF cm ⁻² @ 20 mA cm ⁻² ; ~97.7 % retention after 2000 cycles	One-step hydrothermal growth on Fe foil enabled binder-free electrode architecture	[96]

Following the discussion of graphene–metal oxide nanocomposites, it is important to visualize how these materials are structurally integrated at the nanoscale. Graphene-based systems typically comprise layered carbon frameworks functionalized with oxygen-containing groups that serve as anchoring sites for metal oxide nanoparticles. A representative schematic illustrating the incorporation of various metal oxides onto graphene sheets is presented in Figure 4.

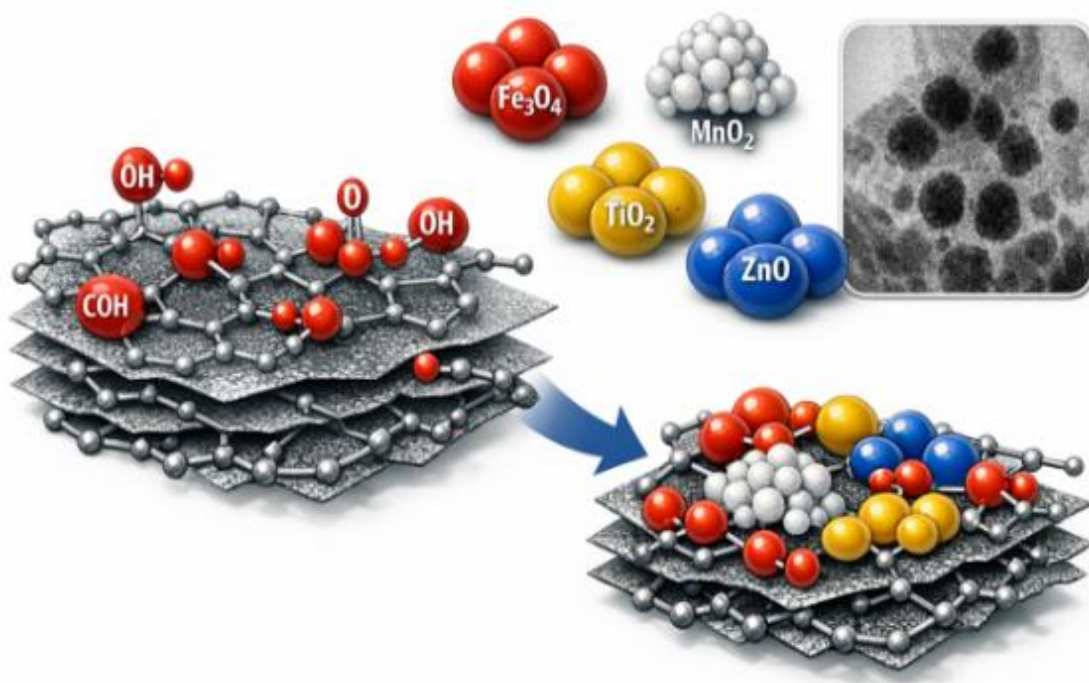


Figure 4. Schematic illustration of graphene-based nanocomposite structures showing the incorporation of metal oxide nanoparticles (e.g., Fe_3O_4 , MnO_2 , TiO_2 , ZnO) onto functionalized graphene sheets, highlighting the role of surface groups in nanoparticle anchoring and dispersion.

2.7.4 Research Gaps and Opportunities

Despite significant advancements, several gaps remain. Some of these gaps are:

Standardized comparisons. Testing conditions vary greatly across studies — such as the type of electrolyte used (the liquid or solid that moves ions between electrodes in a device), current density (the amount of electric current flowing per unit area of electrode), and electrode mass loading (the

amount of active material loaded onto each electrode). This makes direct comparison difficult. Careful benchmarking under identical conditions is needed.

Biomass-derived carbon integration. Many studies on the application of graphene nanocomposites use graphene derived from conventional synthetic sources. Studies that specifically integrate biomass-derived graphene or GLC with $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ and SiO_2 remain limited. This represents a clear opportunity to explore how biomass microstructure and activation history affect composite performance.

Morphology control. How do nanoparticle size, dispersion, and crystallographic phase influence electrochemical behavior? Systematic studies on this question — especially in ternary systems such as $\text{NS-GLC}@ \text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4 @ \text{SiO}_2$ — remain underdeveloped.

Mechanistic understanding. Although synergistic enhancement is frequently reported, comprehensive mechanistic insight into ion transport pathways and the interplay between EDLC and pseudocapacitance at the nanoscale requires further experimental and theoretical investigation. This is another research gap worth exploring.

Addressing these gaps requires improved material design, yes. But also a systematic and comparable electrochemical assessment. By closing these research gaps, we can more effectively correlate structural features with performance metrics across different graphene-based systems, thereby building a solid foundation for further electrochemical evaluation.

2.8 Electrochemical Evaluation

Assessing the suitability of graphene-based materials for energy storage requires evaluating electrochemical properties — particularly in relation to structural, functional, and morphological characteristics. Structural and morphological characterization provides foundational information.

Electrochemical testing, however, directly determines how the material performs in practical devices.

For biomass-derived graphene and its nanocomposites, electrochemical evaluation serves an additional purpose: it enables the correlation of synthesis parameters, pore structure, surface chemistry, and conductivity with actual charge storage performance.

In this study, the electrochemical performance is investigated primarily in the context of supercapacitors. Both EDLC and pseudocapacitive mechanisms contribute to overall energy storage.

2.8.1 Supercapacitor Basics

Supercapacitors, also referred to as electrochemical capacitors, are energy storage devices characterized by high power density, rapid charge-discharge capability, and extended cycle life [5, 54].

In contrast to batteries, which rely on bulk redox reactions and relatively slow ion diffusion within electrode materials, supercapacitors store energy through surface or near-surface processes, resulting in substantially faster kinetics. However, this comes at the cost of a lower energy density than batteries. Consequently, supercapacitors are most suitable for applications requiring high power delivery and rapid cycling, rather than long-term energy storage. Charge storage in supercapacitors happens through two main mechanisms: electric double-layer capacitance (EDLC) and pseudocapacitance [54, 58]. EDLC is charge separation at the electrode-electrolyte interface, whereas pseudocapacitance involves fast surface redox reactions.

EDLC comes from the electrostatic accumulation of ions at the electrode-electrolyte interface without charge transfer across the interface. The process is highly reversible and depends strongly

on the accessible surface area and pore structure of the electrode material. Graphene and graphene-like carbon materials perform particularly well in EDLCs. The reason for this is their inherent properties such as high specific surface area, excellent electrical conductivity, and chemical stability [4, 7]. Pseudocapacitance, on the other hand, is different. It involves fast, reversible faradaic reactions at or near the electrode surface [5]. These reactions are typically associated with transition metal oxides or heteroatom-doped carbon materials. Examples: nitrogen and sulfur doping introduce functional groups and defects that can participate in redox reactions, thereby adding capacitance beyond that of pure EDLC [78, 79]. Similarly, metal oxides such as Fe_2O_3 and Fe_3O_4 provide redox-active sites that enhance charge storage via reversible oxidation-reduction processes [88, 101]. In practical electrode systems — especially graphene-based composites — both EDLC and pseudocapacitance contribute simultaneously. The relative contribution of each depends on material composition, surface functionalization, electrolyte type, and operating potential window. Getting the right balance between these mechanisms is essential for maximizing both energy and power density.

The Ragone plot (Figure 5) is often used to illustrate the performance of electrochemical energy storage devices. A Ragone plot shows the relationship between energy density (how much energy can be stored per unit weight or volume) and power density (how quickly energy can be delivered per unit weight or volume). This plot provides a convenient means of comparing different energy storage technologies, highlighting the trade-off between energy storage capacity and power delivery capability. Batteries are known to demonstrate high energy density but relatively low power density, reflecting slower kinetics. Supercapacitors, on the other hand, possess high power density but moderate energy density [58]. Hybrid systems and advanced nanocomposites aim to bridge this divide by integrating both capacitive and faradaic mechanisms.

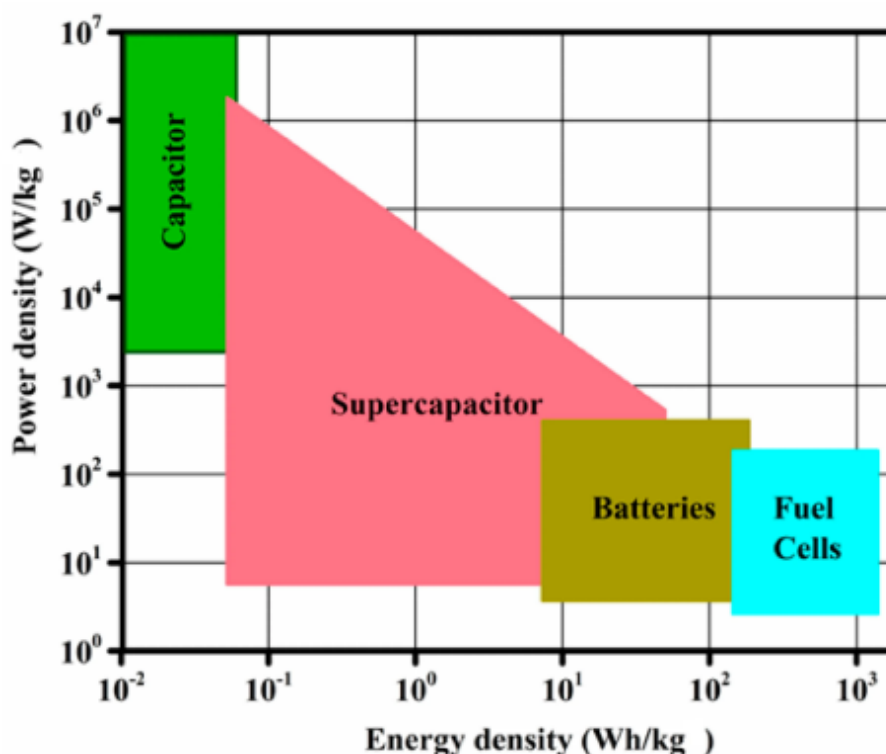


Figure 5. Ragone plot showing the relationship between energy density and power density for conventional capacitors, supercapacitors, and batteries. The figure highlights the position of supercapacitors between high-power capacitors and high-energy batteries, demonstrating the trade-off between energy storage capacity and power delivery [102].

Figure 5 compares batteries, conventional capacitors, and supercapacitors. It shows where supercapacitors sit — in the middle. It also hints at how better materials could push their performance further. This figure helps explain why graphene-based materials matter for advancing supercapacitor technology.

2.8.2 Performance Metrics and Testing

Several techniques are typically used to determine if a graphene-based material is suitable for energy storage. The most common ones are cyclic voltammetry (CV, which measures the current response as the voltage is swept), galvanostatic charge-discharge (GCD, which assesses material performance by charging and discharging at constant current), and electrochemical impedance

spectroscopy (EIS, which examines resistance and capacitance by applying an alternating voltage). Each of these techniques offers distinct insights into charge storage behavior, kinetics, and internal resistance [53].

Cyclic voltammetry (CV) is widely used to elucidate charge-storage mechanisms and electrochemical reversibility. In an ideal EDLC system, CV curves look nearly rectangular. That shape means rapid ion adsorption and desorption with minimal resistive losses. If the curve deviates from a rectangle — say, redox peaks show up — that suggests pseudocapacitive contributions. For graphene-based composites, CV is especially useful. This is because it helps in separating EDLC behavior from the carbon matrix. In addition, it distinguishes faradaic contributions from dopants or metal oxides. How CV curves change with scan rate indicates rate capability and ion transport. If the shape holds up at high scan rates, that means efficient ion diffusion and low resistance [5, 53].

Galvanostatic charge-discharge (GCD), on the other hand, provides quantitative evaluation of capacitance and energy storage. In EDLC-dominated systems, GCD curves are typically triangular and symmetric. Constant current charging and discharging, with minimal voltage drop. When a plateau or deviation from linearity is observed, this usually indicates faradaic reactions associated with pseudocapacitance. From GCD data, specific capacitance, energy density, and power density can be calculated.

This, in turn, helps determine the cycling stability of the active material in supercapacitor settings. Specific capacitance usually comes from the discharge slope. Energy density and power density are defined using standard electrochemical relations. These parameters are essential for comparing materials and deciding if they're practical [5].

Electrochemical impedance spectroscopy (EIS) further complements these other techniques by revealing details about resistive and capacitive behavior across a range of frequencies. EIS data usually show up as Nyquist plots. The high-frequency region reflects solution resistance and charge-transfer resistance. The low-frequency region matches capacitive behavior and ion diffusion. A small semicircle in the high-frequency region indicates charge-transfer resistance. A nearly vertical line at low frequencies means close to ideal capacitive behavior.

For graphene-based nanocomposites, EIS is particularly important. It helps enable the understanding of how structural features — porosity, particle dispersion, interfacial contact — affect charge transport.

Alongside these electrochemical analyses, several performance metrics also warrant attention.

Specific capacitance, measured in farads per gram (F g^{-1}), is the most reported parameter. It reflects the charge storage capacity per unit mass of active material. Energy density (Wh kg^{-1}) and power density (W kg^{-1}) give a broader view of device performance. These metrics are often used with Ragone plots.

Cycling stability—usually expressed as the percentage of capacitance retained after thousands of charge-discharge cycles—is critical for assessing long-term performance and whether a material could actually be used.

Biomass-derived materials add extra considerations. The precursor and synthesis process introduce variability. Pore size distribution, degree of graphitization, and surface functionalization all significantly influence electrochemical behavior.

For example, a large number of micropores increases surface area and boosts EDLC. Mesopores help ion transport and improve rate capability [20]. Heteroatom doping can enhance wettability and introduce pseudocapacitive sites. Too many defects reduce electrical conductivity [78, 79].

For a meaningful comparison between two or more materials, standardization of testing conditions matters. This includes the type of electrolyte (the liquid or gel that conducts ions), the potential window (the range of applied voltages), the current density (current per unit area), and the electrode mass loading (the amount of active material per electrode). If this is not done, it can dramatically affect reported performance metrics [53]. For instance, aqueous electrolytes are known to offer higher ionic conductivity but a limited voltage window. Organic electrolytes allow higher operating voltages. However, they may have lower conductivity and larger ion sizes. So, a material optimized for one electrolyte system may not perform well in another [6].

In this study, electrochemical evaluation is done primarily with supercapacitor configurations. That reflects the structural characteristics of the synthesized materials. These materials favor capacitive behavior. The combination of graphene-like carbon, heteroatom doping, and metal oxide integration should produce electrodes that show both EDLC and pseudocapacitive contributions. The result is better overall performance.

Using multiple electrochemical techniques ensures a comprehensive understanding of charge storage mechanisms. It also allows correlation of material properties with electrochemical behavior.

Taken together, these evaluation approaches do two things. They provide performance metrics for the developed materials. They also establish a framework for understanding how structural and compositional modifications influence electrochemical behavior in graphene-based systems.

2.9 Summary of Literature Gaps

Several gaps persist in the graphene-based energy-storage literature. They point to a need for approaches that connect the different synthesis routes instead of treating them as separate worlds.

One major issue is the disconnect between the main pathways used to produce graphene-based carbon materials. On one side, graphene-like carbon (GLC) is produced through catalytic graphitization, while on the other, graphene oxide (GO) is obtained through chemical oxidation. Most studies focus on one of these approaches rather than considering both. They either investigate graphitized carbons or GO-derived materials, with relatively few studies making a direct comparison between the two. There are also limited studies that combine these approaches in a controlled way. As a result, it is still not clear how the differences in these production pathways affect the resulting structure and, in turn, the electrochemical behaviour of the materials.

A second gap arises from how synthesis parameters are optimized. Researchers do explore variables — catalyst choice, activation method, doping conditions — but usually one at a time. These factors are rarely studied as part of a connected sequence. For example, a clear mechanism of how iron catalysts, chemical activation agents, and heteroatom doping interact to influence graphitization, pore development, or performance is still being studied and understood. Without that kind of coordinated optimization, it is difficult to map out reliable structure–property–performance relationships.

The third limitation is the inconsistent exploration of activation strategies. There is a balance between conventional single-agent activation, like KOH, and alternative or combined methods using phosphoric acid or zinc chloride. These methods have been studied individually. Their comparative effectiveness and potential synergistic effects, though, have not been

comprehensively evaluated for biomass-derived graphene materials. Challenges with cost, chemical consumption, and process complexity are often overlooked — even though they matter for practical implementation.

The fourth unresolved area is heteroatom doping, particularly the incorporation of nitrogen and sulfur. Many studies report improved electrochemical performance after doping, but the factors responsible for this improvement are not yet fully understood. The doping method, whether hydrothermal or thermal, can affect the amount and distribution of the dopant as well as its bonding configuration within the carbon structure. Dopant concentration is also important, since a higher dopant content does not necessarily lead to better electrochemical performance and may introduce excessive defects or reduce electrical conductivity. In addition, the relationship between heteroatom doping, defect formation, and conductivity is still not clearly established. A better understanding of these effects is therefore needed to determine how doping conditions influence the resulting charge storage behaviour and to allow more consistent control over the properties of the carbon material.

The fifth gap concerns graphene-based nanocomposites. The integration of metal oxides, such as iron oxides, has shown promising improvements in pseudocapacitive behavior. But understanding of how composite architecture, particle dispersion, and interfacial interactions affect long-term stability and rate capability is still limited. Still limited. Also, structural modifications to components like SiO_2 are often discussed in qualitative terms — "improves stability" — without sufficient quantitative analysis of their actual impact on pore structure and ion transport.

The sixth critical gap borders on scalable, environmentally sustainable, and effective electrode materials. Many reported synthesis methods rely on harsh chemicals or multi-step procedures. Some rely on conditions that are difficult to scale, which limits practical applicability. The use of

renewable biomass precursors with optimized synthesis and functionalization strategies remains underexplored, despite their potential for sustainable production.

Addressing these gaps calls for a holistic approach: multiple synthesis pathways should be integrated, systematic optimization techniques should be applied, and clear relationships between material structure and electrochemical performance should be established.

Accordingly, this study is designed to tackle these challenges by combining biomass-derived graphene synthesis routes, optimization methodologies, and functional modifications within a unified framework for high-performance supercapacitor applications. Thus, the strategies proposed here directly address the limitations identified in the literature, forming the foundation for the experimental framework presented in the following chapters.

2.10. Chapter Summary

The literature reviewed in this chapter highlights how far research on graphene-based materials for electrochemical energy storage has come—and where it still falls short. There have been impressive advances in areas like biomass-derived carbons, catalytic graphitization, graphene oxide synthesis, heteroatom doping, and nanocomposite design. Even so, key challenges remain. For example, researchers still need to develop more integrated synthesis strategies and apply comprehensive optimization across each step of the process. There's also a need to better understand how the choices made during synthesis affect the structure of the material—and, in turn, how that structure influences its electrochemical performance.

The present study adopts a comprehensive and systematic experimental approach that integrates multiple synthesis pathways and optimization strategies within a unified framework to try to address these challenges. Specifically, the study combines catalytic graphitization and chemical

activation routes in a single process to produce graphene-like carbon, with controlled synthesis of graphene oxide and its derivatives, followed by targeted doping and nanocomposite fabrication.

Finally, Chapter 3 covers the materials, experimental procedures, and overall research design employed in this work. It details the selection of biomass precursors, synthesis methodologies, optimization strategies, and characterization techniques used to investigate the structure–property–performance relationships of the developed materials. This experimental framework forms the basis for the results and discussions presented in the subsequent chapters.

3. MATERIALS AND EXPERIMENTAL DESIGN

3.1 Materials

Hazelnut shell biomass was used as the primary carbon precursor for synthesizing graphene-based materials. The biomass was chosen because it has a high fixed-carbon content and a favorable lignocellulosic composition, which facilitates the formation of graphitic structures during thermochemical conversion.

For the synthesis of graphene-like carbon via catalytic graphitization, iron-based catalysts were used. Ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) and ferric chloride (FeCl_3) were used in separate synthesis routes as alternative catalyst systems to evaluate their effectiveness in promoting graphitic domain development. Potassium hydroxide (KOH) served as the primary chemical activating agent for the development of porosity and enhancement of surface area. In selected exploratory experiments, zinc chloride (ZnCl_2) and phosphoric acid (H_3PO_4) were also utilized to investigate alternative activation routes and their influence on pore structure.

For the synthesis of graphene oxide (GO), concentrated sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), boric acid (H_3BO_3), and potassium permanganate (KMnO_4) were used as oxidizing and reaction media components in modified Hummers-based methods. Reduction of GO was carried out using ascorbic acid as a chemical reducing agent and by thermal treatment under regulated conditions.

Thiourea was used as the precursor for nitrogen and sulfur co-doping of graphene-based materials. Both hydrothermal and thermal doping approaches were used to investigate the influence of processing conditions on dopant incorporation and material structure, and to enable comparison of mild and high-temperature functionalization routes. Also, silicon dioxide (SiO_2) nanopowder and

ferric chloride were used as reagents to form graphene-based hybrid structures during the nanocomposite fabrication phase. Ferric chloride solution was used to introduce Fe species into the mix. This step was followed by thermal treatment to form iron oxide phases within the composite matrix.

All chemicals used in this study were of analytical grade and were used as received without further purification. Deionized water was used throughout all experimental procedures.

3.2 Experimental Design and Optimization Strategy

The experimental design adopted in this study was developed to enable a systematic investigation of biomass-derived graphene-based materials through a multi-stage synthesis and modification framework. Two primary synthesis pathways were employed: graphene-like carbon (GLC) produced via catalytic graphitization and chemical activation, and graphene oxide (GO) obtained through chemical oxidation of graphitized biomass. These materials were subsequently subjected to reduction, heteroatom doping, nanocomposite fabrication, and electrochemical evaluation.

A schematic overview of the experimental workflow is presented in the literature review (Figure 2.1) and is therefore not repeated here.

The study is structured as a hierarchical experimental framework in which synthesis pathways are progressively refined from biomass-derived carbon production to chemical modification, enabling controlled comparison and optimization of structural changes across all stages.

To systematically optimize synthesis parameters, the Taguchi method was employed as the primary experimental design approach. This statistical technique used orthogonal arrays to evaluate the influence of multiple factors with fewer experiments than conventional full factorial designs. In this study, L9 orthogonal arrays were used across all optimization stages, enabling efficient

investigation of key parameters in GLC synthesis, GO production, and heteroatom doping while maintaining statistical balance and experimental efficiency.

3.2.1 Selection of Factors and Levels

The selection of factors and levels for each optimization stage was guided by prior literature [103], preliminary experiments, and the known influence of these factors on the structural and electrochemical properties of carbon materials.

For the synthesis of graphene-like carbon, four key parameters were selected based on Nwodika et al [104]: biochar particle size, KOH-to-biochar ratio, ferrocene catalyst dosage, and final pyrolysis temperature. These factors govern critical aspects of material formation, including carbon rearrangement, pore development, and degree of graphitization. The corresponding levels for each parameter are summarized in Table 6.

Table 6. Factors and levels for Taguchi optimization of graphene-like carbon synthesis. Reproduced from Nwodika et al. [104].

Factor	Parameter	Levels (L ₁ , L ₂ , L ₃)
A	Biochar Particle Size (μm)	75, 97, 125
B	KOH:Biochar (w/w)	1:1, 2:1, 3:1
C	Ferrocene Dosage (% relative to biochar)	10%, 15%, 20%
D	Pyrolysis Temperature (°C)	800, 900, 1000

For graphene oxide synthesis, four parameters were considered: potassium permanganate dosage, acid composition ratio, oxidation temperature, and reaction time. These variables directly influence the degree of oxidation, defect generation, and functional group incorporation. The selected levels are presented in Table 7.

Table 7: Factors and levels for Taguchi optimization of graphene oxide synthesis

Factor	Parameter	Levels (L ₁ , L ₂ , L ₃)
A	KMnO ₄ Dosage (g)	2, 3, 4
B	Acid Ratio (H ₂ SO ₄ :H ₃ PO ₄)	3:1, 6:1, 9:1
C	Oxidation Temperature (°C)	40, 50, 60
D	Oxidation Time (h)	6, 9, 12

For heteroatom doping, a three-factor design was adopted to evaluate the hydrothermal incorporation of nitrogen and sulfur using thiourea. The parameters investigated were thiourea dosage, reaction temperature, and reaction time, which determine dopant incorporation efficiency and structural modification. The selected levels are summarized in Table 8.

Table 8: Factors and levels for Taguchi optimization of heteroatom doping

Factor	Parameter	Levels (L ₁ , L ₂ , L ₃)
A	Thiourea Dosage (g)	2, 3, 4
B	Oxidation Temperature (°C)	160, 180, 200
C	Doping Residence Time (h)	6, 12, 24

The coded experimental layouts based on L9 orthogonal arrays were used to assign combinations of factor levels across all experimental runs. These designs ensure probabilistic independence of variables and allow efficient evaluation of individual factor effects. The corresponding experimental conditions and results are presented and discussed in Chapter 4.

3.2.2 Multi-Response Optimization Using Grey Relational Analysis

The optimization of synthesis parameters involved multiple response variables, requiring simultaneous evaluation of structural, compositional, and performance-related properties. Since single-response optimization cannot adequately account for trade-offs among competing objectives, Grey Relational Analysis (GRA) was used alongside the Taguchi method for multi-response optimization.

GRA converts multiple response variables into a single grey relational grade, allowing comprehensive evaluation of overall material performance.

For graphene-like carbon (GLC) optimization, the evaluated responses included BET surface area, yield, thermal stability, and Raman I_D/I_G ratio. These parameters were selected to represent porosity development, carbon structure ordering, and thermal robustness.

Experimental data for GLC were normalized using appropriate criteria: "larger-the-better" for BET surface area, yield, and thermal stability; and "smaller-the-better" for Raman I_D/I_G ratio.

For graphene oxide (GO) optimization, two response parameters were considered: the oxygen-to-carbon (O/C) ratio and the Raman I_D/I_G ratio. The O/C ratio was used as an indicator of oxidation level and functional group incorporation, with a target near 0.5 representing balanced oxidation ("nominal-the-best"). The I_D/I_G ratio was used as an indicator of defect density and structural disorder ("smaller-the-better"), indicating the degree of graphitic degradation during oxidation.

Grey relational coefficients were then calculated for each response and combined to obtain a grey relational grade for each experimental run. In each material system (GLC and GO), weighting factors were assigned to the selected responses to reflect their relative influence on structural and electrochemical performance, as defined in the experimental design framework and reported in the respective optimization sections.

The combination of GRA and the Taguchi method enabled the identification of locally optimal synthesis conditions for each material system while accounting for multiple performance criteria.

3.2.3 Integration of Optimization Across Experimental Stages

A key feature of this research is the structured integration of optimization through multiple stages of material development. Rather than treating each synthesis step as an isolated process, a hierarchical experimental strategy was adopted in which preliminary screening, statistical optimization, and application-oriented synthesis were systematically connected. Initial exploratory experiments were used to identify suitable processing windows and establish reproducible baseline conditions for each synthesis route. These screening outcomes were not treated as optimized results but as guidance for defining controlled conditions for subsequent statistical design.

The Taguchi–Grey Relational Analysis framework was then applied within each material system to optimize key synthesis parameters under fixed baseline conditions. This ensured that the influence of individual controllable factors could be isolated and evaluated with statistical thoroughness.

Following optimization, the resulting parameter findings were selectively carried forward into subsequent synthesis stages. However, final material synthesis decisions were additionally guided by feasible considerations such as scalability, precursor availability, and process stability. This means that while statistical optimization informed parameter identification, it was not the sole determinant of all later-stage synthesis conditions. This multi-level approach enables consistency throughout the experimental workflow while allowing flexibility in translating processes from optimized laboratory-scale conditions to practical material fabrication. It also enables clear correlation between synthesis parameters, structural development, and functional properties across all stages of material development.

3.2.4 Link to Electrochemical Performance

While the optimization procedures in this study focus primarily on material-level properties such as surface area, structural order, and elemental composition, these parameters are closely linked to electrochemical behavior. Increased surface area enhances charge storage capacity, improved graphitization raises electrical conductivity, and heteroatom doping introduces additional active sites and pseudocapacitive contributions.

Optimizing these structural and compositional features establishes a foundation for improved electrochemical performance, which is evaluated in detail during electrochemical characterization of each material system. This approach ensures a focused, methodologically consistent optimization strategy that aligns with the overall objective of developing electrode materials for energy storage applications such as supercapacitors.

3.3 Synthesis of Graphene-Like Carbon (GLC)

3.3.1 Preparation of Biomass Precursor

The method used here is as reported by Nwodika et al [104]. Hazelnut shell biomass was used as the carbon precursor due to its high fixed carbon content and lignocellulosic composition, which are favorable for the formation of graphitic carbon architectures during thermochemical conversion. Before processing, the raw hazelnut shells were manually cleaned to remove surface impurities and contaminants, then dried to eliminate residual moisture that could interfere with thermal treatment and chemical impregnation.

The dried biomass was mechanically ground to obtain a fine powder, thereby increasing surface area and improving interactions with activating agents and catalysts during subsequent processing. The ground material was then sieved into controlled particle size fractions of 75 μm , 97 μm , and 125 μm , corresponding to the levels defined in the Taguchi experimental design. Controlling

particle size is critical because it affects heat transfer, the diffusion of activating agents, and the uniformity of carbonization and graphitization. Smaller particle sizes generally enhance reactivity and facilitate more uniform activation, while larger particles may limit penetration of activating agents and lead to heterogeneous structures.

The prepared biomass fractions were stored in sealed containers under ambient conditions to prevent moisture reabsorption prior to impregnation and thermal treatment.

3.3.2 Impregnation with Activating Agent and Catalyst

The synthesis of graphene-like carbon in this study was based on a one-step integrated approach merging chemical activation and catalytic graphitization, in which the carbon precursor was simultaneously treated with an activating agent and an iron-based catalyst prior to pyrolysis.

Potassium hydroxide (KOH) was employed as the primary activating agent due to its strong ability to generate porous carbon structures. During high-temperature treatment, KOH reacts with carbon to form metallic potassium, potassium oxides, and gaseous species (CO and CO₂), which contribute to the development of microporous and mesoporous structures. The KOH-to-biochar ratio was varied at 1:1, 2:1, and 3:1 (w/w) in accordance with the Taguchi design to evaluate its influence on pore development and surface area [104].

Iron-based catalysts were introduced to promote catalytic graphitization, facilitating the transformation of amorphous carbon into more ordered graphitic domains. Two catalyst systems were investigated: ferrocene and ferric chloride (FeCl₃).

Ferrocene was primarily used during the Taguchi optimization stage as a model catalyst system due to its well-defined decomposition behavior and ability to generate uniformly dispersed iron nanoparticles under controlled conditions, ensuring reproducibility and statistical validity during

the design of experiments (Taguchi analysis), where sensitivity to synthesis parameters was the primary focus, and this configuration is referred to as CA-GLC (chemically activated graphene-like carbon).

Following completion of the optimization process phase, ferric chloride (FeCl_3) was used in subsequent synthesis stages to evaluate process scalability and precursor compatibility under solution-based impregnation conditions, which are more suitable for extended material development and composite fabrication. FeCl_3 can be readily dissolved and uniformly distributed within the carbon precursor matrix, facilitating effective contact between catalytic species and carbon during thermal treatment. Upon heating, FeCl_3 is converted to iron or iron oxide species that catalyze graphitization via dissolution–precipitation and carbon diffusion mechanisms.

The impregnation process involved intensive mixing of the biomass-derived carbon with KOH and the selected catalyst to ensure homogeneous distribution. For FeCl_3 , solution impregnation was employed, followed by drying to remove solvent and achieve uniform coating. Ferrocene was incorporated via direct mixing or dispersion.

In addition to the primary KOH-based activation system, exploratory experiments were performed using alternative activating agents, including phosphoric acid (H_3PO_4) and zinc chloride (ZnCl_2), either individually or in combination with the iron catalyst. These systems were investigated to assess their influence on pore structure and surface functionality; however, they were not included in the main optimization system and are treated as supplementary to the primary KOH-based approach.

After impregnation, the samples were dried under regulated conditions to remove residual moisture and stabilize the precursor mixture prior to pyrolysis. This step guarantees consistent thermal behavior and prevents uncontrolled reactions during heating.

The combined use of chemical activation and catalytic graphitization in a single processing step is a key feature of this methodology, enabling the simultaneous development of hierarchical porosity and graphitic structure, both essential for enhanced electrochemical performance.

3.3.3 Pyrolysis and Catalytic Graphitization

The conversion of the impregnated biomass precursor into graphene-like carbon was achieved via controlled pyrolysis under an inert atmosphere, integrating chemical activation and catalytic graphitization into a unified thermal process. This approach enables simultaneous pore development and structural ordering, both of which are essential for electrochemical performance.

Following impregnation and drying, approximately 5 g of the prepared precursor mixture (biochar, KOH, and catalyst) was transferred into a lidded alumina crucible to limit direct exposure to the furnace environment while permitting controlled gas exchange. The crucible was then placed in a tubular furnace system. Prior to heating, the furnace was purged with high-purity nitrogen gas for approximately 30 minutes to remove residual oxygen and establish an inert atmosphere. This step prevents unwanted oxidation reactions and ensures controlled carbonization and structural transformation. A continuous nitrogen flow was maintained throughout the thermal treatment. The samples were heated at a controlled rate of $5\text{ }^{\circ}\text{C min}^{-1}$ to the target temperatures (800 $^{\circ}\text{C}$, 900 $^{\circ}\text{C}$, or 1000 $^{\circ}\text{C}$), as defined in the experimental design. Upon reaching the final temperature, the samples were held isothermally for 2 hours to allow sufficient time for activation reactions and catalytic graphitization.

During pyrolysis, KOH reacts with carbon to form potassium-containing intermediates and gaseous species (CO and CO₂), which contribute to the development of hierarchical porosity through chemical etching and gasification. Simultaneously, iron-based catalysts promote graphitization via a dissolution–precipitation mechanism, in which carbon dissolves into metallic iron at elevated temperatures and re-precipitates as graphitic layers upon cooling. The interaction between chemical activation and catalytic graphitization determines the final balance between porosity and structural ordering. This proportion is strongly influenced by temperature and catalyst dispersion, making thermal treatment a critical stage in defining the material structure.

After completion of pyrolysis, the furnace was allowed to cool naturally to room temperature under continuous nitrogen flow to prevent oxidation of the formed carbon structure. The resulting material, containing residual activating agents and inorganic species, was subsequently purified as described in later sections.

3.3.4 Preliminary Investigation of Residence Time and Heating Profile

Before the Taguchi optimization of graphene-like carbon synthesis, preliminary screening experiments were conducted to evaluate the influence of the thermal residence profile on activation and graphitization behavior. The objective was to establish a suitable and reproducible baseline pyrolysis protocol for ensuing statistical optimization studies.

Biochar produced at 500 °C was used as the carbon precursor. For each experiment, 5 g of biochar was impregnated with 20 g KOH and FeCl₃, corresponding to approximately 0.5 g Fe, following the impregnation procedures described in Sections 3.3.2 and 3.3.3. After drying, the samples were pyrolyzed under a nitrogen atmosphere at a heating rate of 5 °C min⁻¹ using the thermal residence profiles defined in Table 9.

Table 9: Preliminary thermal residence profiles investigated prior to Taguchi optimization

Sample Code	Heating Profile	Final Holding Condition
GLC-R1	Direct heating to 900 °C	90 min at 900 °C
GLC-R2	Heating to 400 °C for 60 min, followed by heating to 900 °C	90 min at 900 °C
GLC-R3	Heating to 400 °C for 60 min, then to 800 °C for 60 min, followed by heating to 900 °C	30 min at 900 °C

The investigated profiles included direct heating and staged heating routes that incorporated intermediate isothermal steps before reaching the final temperature. These setups were designed to assess the effect of thermal stabilization steps on carbon restructuring and catalyst-assisted graphitization under otherwise identical chemical conditions. After pyrolysis, all samples were cooled to room temperature under a continuous nitrogen atmosphere to prevent oxidation of the resulting carbon structure. The resulting materials were subsequently purified using the post-treatment procedures described later in Section 3.3.6.

Of the three investigated profiles listed in Table 3.4, the single-step heating protocol (GLC-R1) was selected as the baseline condition for the Taguchi optimization experiments. This selection was made based on process simplicity, reproducibility, and the need to minimize additional thermal variables that could confound the statistical evaluation of the primary synthesis factors.

Using this baseline heating profile enabled the subsequent Taguchi optimization to focus exclusively on the defined controllable parameters (particle size, KOH-to-biochar ratio, catalyst dosage, and final temperature), thereby maintaining statistical validity and comparability across all experimental runs.

3.3.5 Taguchi Experimental Design for GLC

To methodically evaluate the influence of synthesis parameters on the properties of graphene-like carbon, the Taguchi method was employed as the experimental design framework. This approach allows the efficient investigation of multiple factors with fewer experimental runs while ensuring statistical balance and independence among variables.

An L9 orthogonal array was selected for this study; this corresponds to a four-factor at three-level design. The choice of the L9 design allows evaluation of the main effects of each parameter with only 9 experimental runs, considerably reducing experimental complexity compared with a full factorial design.

The factors and levels considered for the optimization of graphene-like carbon synthesis are presented in Table 3.1. These parameters were selected based on their known influence on carbon structure development, pore formation, and catalytic graphitization behavior.

The experimental factors include:

- Biochar particle size, which affects heat transfer and reagent accessibility
- KOH-to-biochar ratio, which governs the extent of chemical activation and pore development
- Ferrocene dosage, which determines the availability of catalytic iron species for graphitization
- Pyrolysis temperature, which influences both activation reactions and structural ordering

The coded L9 orthogonal array used to design the experimental runs is presented in Table 10.

Table 10: L9 orthogonal array (coded levels) for GLC synthesis

Run	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Each experimental run corresponds to a unique combination of factor levels, ensuring that the effects of individual parameters can be independently evaluated. The use of coded levels (L1, L2, L3) eases analysis and facilitates systematic comparison of parameter influence, with the Taguchi optimization stage, carried out using ferrocene as the catalyst precursor, providing a controlled system for statistical evaluation of synthesis parameters. The resulting trends were used to guide later stages of synthesis, and additional process modifications were introduced as needed for subsequent material development.

The experimental results obtained from these runs—including yield, BET surface area, Raman I_D/I_G ratio, and thermal stability—were analyzed using Grey Relational Analysis (GRA) to enable multi-response optimization. This procedure allows simultaneous assessment of multiple performance indicators, ensuring that the selected synthesis conditions reflect an overall improvement in material properties rather than the optimization of a single parameter.

The thorough experimental conditions and corresponding responses are presented in Chapter 4.

3.3.6 Post-Treatment and Washing

Following pyrolysis and catalytic graphitization, the obtained carbon material contained residual inorganic species, including unreacted activating agents, potassium compounds, and iron-based catalyst residues. Effective post-treatment was therefore necessary to purify the material and enable accurate evaluation of its structural and electrochemical properties.

The as-synthesized product was first washed with 2.0 M hydrochloric acid (HCl) to dissolve residual metallic species and inorganic salts. To further enhance metal removal, especially for iron species that may be embedded within the carbon matrix, ethylenediaminetetraacetic acid (EDTA-Na₂) was employed as a chelating agent. EDTA forms stable complexes with iron ions, facilitating effective extraction of residual catalyst species that are not readily removed by acid washing alone. This additional treatment step improves the purity of the carbon material and lowers the likelihood of residual metal interference in electrochemical measurements. These two chemical treatments were followed by water and ethanol washing before drying the resulting material at 100°C overnight.

3.3.7 Alternative Activation and Catalytic Reconstruction Pathways

In addition to the primary KOH-based activation incorporated graphitization, exploratory investigations were performed using phosphoric acid (H₃PO₄) activation combined with ferrocene-catalyzed thermal reconstruction, with and without ZnCl₂-assisted secondary activation. Unlike the main synthesis pathway based on direct biochar activation, this alternative route involved hydrothermal carbonization followed by phosphoric acid activation prior to high-temperature catalytic treatment. H₃PO₄ activation promoted the development of thermally stable porous carbon

structures, while ZnCl_2 -assisted reconstruction further evolved pores during catalytic graphitization.

For clarity, the hydrothermal carbon precursor, phosphoric acid-activated carbon, Fe-reconstructed carbon without ZnCl_2 assistance, and ZnCl_2 -assisted reconstructed carbon are hereafter designated as HTC, HTC-PA, HTC-PA-Fe, and HTC-PA-ZnFe, respectively.

Comparative experiments were also performed in the absence of ZnCl_2 to evaluate its influence on structural development during reconstruction.

These exploratory investigations were conducted to extend the assessment of activation and catalytic reconstruction strategies within the broader study framework. However, they were evaluated independently from the primary Taguchi optimization pathway, which focused on KOH activation and iron-catalyzed graphitization of biochar-derived carbon materials.

After thermal treatment, the samples were thoroughly washed to remove residual salts and metallic species, dried at approximately 105 °C, and stored for subsequent characterization and electrochemical evaluation.

3.4 Synthesis of Graphene Oxide (GO)

3.4.1 Preparation of Biographite Precursor

The synthesis of graphene oxide in this study was based on a biomass-derived graphitic precursor (biographite), prepared through a two-step thermochemical process involving carbonization followed by catalytic graphitization. This approach differs from the simultaneous activation–graphitization route used for graphene-like carbon (Section 3.3) in that it is specifically designed to produce a more ordered carbon structure suitable for chemical oxidation.

Hazelnut shell biomass was first pulverized and sieved to obtain a uniform particle size of approximately 90 μm . The prepared biomass was then carbonized in a tubular furnace under an inert nitrogen atmosphere. The temperature was increased at a controlled heating rate of 5 $^{\circ}\text{C min}^{-1}$ to 500 $^{\circ}\text{C}$, where it was held for 60 minutes to ensure effective decomposition of volatile components and formation of biochar.

The resulting biochar was subsequently used as a precursor for catalytic graphitization. In this stage, the biochar was mixed with ferric chloride (FeCl_3) at a mass ratio of 1:1 (biochar: FeCl_3). The mixture was thoroughly homogenized to ensure uniform distribution of the catalyst within the carbon matrix. This was followed by high-temperature pyrolysis of the mixture under a nitrogen atmosphere. The furnace temperature was increased at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ to 1100 $^{\circ}\text{C}$, followed by a 120-minute isothermal hold. At this elevated temperature, iron species are reduced and act as catalysts for graphitization, promoting the rearrangement of amorphous carbon into more ordered graphitic domains through dissolution–precipitation mechanisms.

After the completion of the thermal treatment, the sample was left in the furnace to enable natural cooling to room temperature under continuous nitrogen flow. The resulting material contained residual iron species, which were removed by acid washing with 2.0 M hydrochloric acid (HCl), water, and ethanol, consistent with the procedure described in Section 3.3, and then dried overnight at 100 $^{\circ}\text{C}$.

The resulting biographite material, characterized by increased structural ordering compared to the initial biochar, was used as the precursor for graphene oxide synthesis via chemical oxidation.

3.4.2. Chemical Oxidation of Biographite and Taguchi Experimental Design

The prepared biographite was oxidized to graphene oxide using a modified Hummers method based on the improved (Tour) protocol, employing a mixed acid system ($\text{H}_2\text{SO}_4\text{:H}_3\text{PO}_4$) without sodium nitrate.

In a typical procedure, biographite was dispersed in a pre-mixed solution of concentrated sulfuric acid and phosphoric acid while continuously stirred. Potassium permanganate (KMnO_4) was gradually added while monitoring the temperature to control the exothermic reaction. The reaction was conducted at predefined temperatures and durations in accordance with the experimental design. Post-oxidation quenching, purification, and drying procedures are described in Section 3.5.

To systematically investigate the influence of process variables, a Taguchi experimental design was used. Four key parameters— KMnO_4 dosage, acid ratio ($\text{H}_2\text{SO}_4\text{:H}_3\text{PO}_4$), reaction temperature, and reaction time—were varied at three levels each using an L9 orthogonal array. The experimental layout followed the coded design presented in Table 10 (the same four-factor–three-level Taguchi design used for GLC optimization was used for GO optimization; hence the reference to the same table), facilitating systematic evaluation of the selected oxidation parameters. For each experimental run, the specified acid ratio, oxidant dosage, and biographite were mixed and stirred at the designated temperature and time.

3.4.3 Boric Acid–Modified Oxidation Method

In addition to the improved Hummers (Tour) method, a boric acid–modified oxidation route was investigated as an alternative oxidation environment for the synthesis of graphene oxide, using the approach of Zhang et al [64], but with some minor modifications.

Typically, biographite and boric acid were mixed at a mass ratio of 1:1 (1 g:1 g), then 50 mL of concentrated sulfuric acid (H_2SO_4) was added. This was followed by the stirring of the mixture in an ice bath for approximately 10 minutes to control the reaction temperature before oxidation. After these 10 minutes, potassium permanganate (KMnO_4) was gradually added into the mixture to maintain the KMnO_4 :biographite ratio at 6:1. The oxidation reaction was conducted at 40 °C for 8 h under continuous stirring. Post-oxidation quenching, purification, and drying procedures followed the procedure described in Section 3.5.

The resulting suspension was centrifuged to separate the oxidized solid material from the acidic reaction medium. The recovered product was then sequentially washed with hydrochloric acid, deionized water, and ethanol before drying under the same conditions as the Tour-method graphene oxide samples. It is referred to as B-GO

The boric acid–modified method was investigated as an alternative oxidation strategy to evaluate the influence of a different acidic environment on the oxidation behavior of biomass-derived graphitic carbon.

3.5 Quenching, Purification, and Reduction of Graphene Oxide

3.5.1 Quenching and Purification of Graphene Oxide

Following oxidation, the reaction mixture was quenched by pouring it into ice to rapidly terminate the oxidation process and dissipate residual heat. For syntheses involving 1 g of biographite, 1 mL of 30% hydrogen peroxide (H_2O_2) was subsequently added to reduce residual manganese species. The suspension was gently stirred to promote complete reaction and homogenization. The resulting graphene oxide (GO) was recovered by centrifugation at 4000 rpm, followed by sequential washing with 2 M hydrochloric acid (HCl), deionized water, further washing with EDTA-Na_2 ,

more deionized water, and ethanol to remove residual salts, acids, and impurities. The purified GO was then dried overnight at 60 °C.

For investigating GO reduction pathways, the synthesized GO was first centrifuged to remove excess reaction residues, then washed twice with deionized water before reduction.

3.5.2 Chemical Reduction Using Ascorbic Acid

To perform the chemical reduction, the GO was first dispersed in deionized water on a hotplate stirrer, and then ascorbic acid was added to the beaker at a weight ratio of 5:1 (ascorbic acid:GO). The suspension was stirred at 80 °C for 6 h to facilitate reduction. The reduced graphene oxide (rGO) was then collected by centrifugation at 4000 rpm and washed sequentially with 1 M HCl and deionized water. Then, EDTA-Na₂ was used to complete the washing, followed by water and ethanol. The product was dried overnight at 80 °C and designated as chemically reduced graphene oxide (CrGO).

3.5.3 Thermal Reduction

For thermal reduction, the pre-washed GO was dried overnight, then transferred into a crucible and placed in a furnace under an inert atmosphere. The sample was heated at a rate of 5 °C min⁻¹ to 700 °C and maintained for 120 min. After cooling naturally to room temperature, the thermally reduced product was purified by washing with 2 M HCl, deionized water, and ethanol, followed by overnight drying at 80 °C. The resulting material was designated as thermally reduced graphene oxide (TrGO).

3.5.4 Combined Chemical–Thermal Reduction

For the sequential chemical–thermal reduction route, the GO was first chemically reduced with ascorbic acid under the same conditions described above, using a 5:1 (w/w) ascorbic acid:GO weight ratio at 80 °C. The difference between this and the chemical reduction pathway lies in the duration of ascorbic acid reduction, which was 3 h, compared with 6 h used earlier. The partially reduced product was centrifuged, washed twice with deionized water to remove residual reagents, and then dried overnight at 80 °C.

Following drying, the partially reduced GO was subsequently thermally reduced in a furnace under an inert atmosphere at 400 °C for 1 h using a heating rate of 5 °C min⁻¹. After cooling naturally, the product was purified by sequential washing with 2 M HCl, deionized water, and ethanol, and finally dried overnight at 80 °C. The resulting material was designated as combined chemically and thermally reduced graphene oxide (CTrGO).

3.6 Heteroatom Doping of Graphene-Like Carbon

3.6.1 Hydrothermal N/S Doping of Graphene-Like Carbon

Initial heteroatom doping studies were conducted via a hydrothermal approach to introduce nitrogen and sulfur groups into graphene-like carbon (GLC). The parent material used for the doping study was produced following the simultaneous catalytic graphitization and secondary chemical activation route described earlier, employing either KOH or ZnCl₂ activation (in separate precursor preparation routes) with ferrocene-assisted graphitization on H₃PO₄-activated carbon. In this dissertation, the material is designated as ferrocene-assisted activated graphene-like carbon (SA-GLC), representing the optimized high-graphitization carbon fractions used for doping studies.

The rationale behind choosing hydrothermal doping as the initial modification strategy is that it promotes surface functionalization under relatively mild conditions and enables intimate interaction between the dopant precursor and the carbon framework. Also, thiourea was chosen as the nitrogen/sulfur precursor because of its dual heteroatom content and widespread use in graphene doping studies.

To methodically evaluate the influence of doping parameters, a Taguchi experimental design consisting of three factors at three levels was employed. The investigated factors were thiourea dosage, doping temperature, and reaction time. The factor levels are presented in Table 11, while the corresponding L9 orthogonal array (coded levels) is shown in Table 3.6.

Table 11: L9 Orthogonal Array (Coded Levels) for Hydrothermal N/S Doping

Run	A	B	C
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

Based on the experimental design, each synthesis run was performed using 1 g of SA-GLC mixed with the required amount of thiourea according to the specified factor level. The mixture was dispersed in a solvent system containing 75 mL of deionized water and 15 mL of ethanol, then sonicated for 60 min to ensure homogeneity. This was followed by transferring the mixture into a Teflon-lined hydrothermal autoclave reactor rated for operation at 3 MPa and 250 °C. Each experimental run was conducted at the designated temperature and duration defined by the Taguchi design.

At the end of the hydrothermal treatment, the reactor was allowed to cool naturally to room temperature. The resulting suspension was centrifuged to remove the supernatant, then sequentially washed with 0.1 M hydrochloric acid, deionized water, and ethanol until a near-neutral pH was achieved. The recovered material was subsequently dried overnight at 80 °C.

The resulting doped materials were designated as hydrothermally doped graphene-like carbon (HD-GLC_i, where i denotes the mass of thiourea used: 2, 3, or 4g).

3.6.2 Thermal N/S Doping of Graphene-Like Carbon

Following the completion of the hydrothermal doping study, a thermal doping strategy was investigated as a more scalable and time-efficient approach to incorporating nitrogen and sulfur functional groups into graphene-like carbon. This transition was introduced to evaluate whether thermal activation could achieve comparable dopant incorporation while improving process scalability and simplifying reaction control.

In this case, the parent graphene-like carbon was synthesized via simultaneous catalytic graphitization and chemical activation of biochar using FeCl₃ and KOH. To distinguish it from the phosphoric acid-activated material used in hydrothermal doping studies, the parent material was designated as chemically activated graphene-like carbon (CA-GLC), while the phosphoric acid-activated material used in Section 3.6.1 was earlier designated as phosphorus-activated graphene-like carbon (SA-GLC) (naming retained as defined for consistency across doping routes).

The same thiourea-to-carbon ratios employed in the hydrothermal study were used for thermal doping, corresponding to thiourea: CA-GLC mass ratios of 2:1, 3:1, and 4:1.

For each synthesis, the required amount of thiourea was mixed with the graphene-like carbon and dispersed in a water-ethanol solvent system, then sonicated for 60 min to promote homogeneous mixing and precursor infiltration. The resulting suspension was dried overnight at 80 °C to remove

residual solvent. The dried material was subsequently transferred into a tube furnace and thermally treated under a continuous nitrogen atmosphere. Pyrolysis was conducted at 700 °C with a heating rate of 5 °C min⁻¹ for 120 min. After thermal treatment, the furnace was allowed to cool naturally to room temperature under nitrogen flow.

The resulting doped material was sequentially washed with 0.1 M hydrochloric acid, deionized water, and ethanol to remove residual impurities and loosely bound species, and then dried overnight at 80 °C.

The resulting materials were designated as thermally doped graphene-like carbon (TD-GLC_i, where i denotes the mass of thiourea used: 2 g, 3 g, or 4g).

3.6.3 Thermal N/S Doping of Combined Chemically and Thermally Reduced Graphene Oxide

Thermal nitrogen/sulfur co-doping was further extended to the combined chemically and thermally reduced graphene oxide (CTrGO) prepared as described earlier. The same doping methodology and thiourea-to-carbon mass ratios as in Section 3.6.2 were employed in this study, corresponding to thiourea: CTrGO ratios of 2:1, 3:1, and 4:1.

Briefly, the required amount of thiourea was mixed with CTrGO in a water–ethanol solvent system and sonicated for 60 min to ensure homogeneous dispersion and effective precursor infiltration. This was followed by the drying of the mixture overnight at 80 °C before thermal treatment. The pyrolysis was conducted in a tube furnace under a continuous nitrogen atmosphere at 700 °C for 120 min at a heating rate of 5 °C min⁻¹, then cooled naturally to room temperature under a nitrogen atmosphere. The resulting material was purified using the same washing procedure described in Section 3.6.2, with hydrochloric acid, deionized water, and ethanol until a near-neutral pH was reached, and then dried overnight at 80 °C.

The materials obtained were designated as thermally doped, combined chemically and thermally reduced graphene oxide (TD-CTrGO_i), where i denotes the mass of thiourea used (2, 3, or 4 g).

3.7 Fabrication of Iron Oxide–SiO₂ Graphene-Based Nanocomposites

Thermally doped graphene-like carbon prepared using 3 g thiourea (TD-GLC₃) and thermally doped combined chemically and thermally reduced graphene oxide prepared using 3 g thiourea (TD-CTrGO₃) were employed as carbon supports for the fabrication of iron oxide–SiO₂ graphene-based nanocomposites. TD-CTrGO₃ was prepared following the same thermal doping procedure described in Section 3.6.2, using combined chemically and thermally reduced graphene oxide (CTrGO) as the parent material.

Initially, three graphene:iron oxide:SiO₂ weight ratios, namely 85:12.5:2.5, 78.5:20:1.5, and 80:15:5, were investigated using TD-GLC₃ as the carbon support. For all syntheses, the mass of the graphene-based support was fixed at 1.10 g. The corresponding FeCl₃ and SiO₂ precursor masses used to obtain the targeted composite compositions are summarized in Table 12.

Depending on the outcome of the electrochemical performance evaluation of the TD-GLC₃-derived nanocomposites, the optimal composition that yielded the best electrochemical performance for the doped rGO sample will be subsequently used to prepare the TD-CTrGO₄-derived nanocomposite, ensuring direct comparability of nanocomposite performance across different carbon support systems under identical compositional conditions.

Table 12: Composition ratios and precursor masses used for iron oxide–SiO₂ nanocomposite synthesis

Graphene support	Graphene support mass (g)	Graphene:Iron oxide:SiO ₂ ratio	FeCl ₃ mass (g)	SiO ₂ mass (g)
TD-GLC ₃	1.10	78.5:20:1.5	0.57	0.021
TD-GLC ₃	1.10	80:15:5	0.42	0.069
TD-GLC ₃	1.10	85:12.5:2.5	0.33	0.032

TD-CTrGO3	1.10	<i>Best-performing TGFS ratio</i>	Corresponding mass	Corresponding mass
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For each synthesis, the required amount of TD-GLC₃ or TD-CTrGO₄ was dispersed with FeCl₃ and SiO₂ in a water–ethanol solvent system, then sonicated to ensure homogeneous mixing and effective infiltration of the precursor onto the graphene surface. The resulting suspension was dried overnight at 80 °C to remove residual solvent.

The dried mixture of the reagents was later transferred into a furnace and thermally treated at 350 °C for 60 min, using 5 °C min⁻¹, under ambient atmospheric conditions (non-inert environment), a deliberate decision to facilitate oxidative decomposition of FeCl₃ into iron oxide phases (Fe₂O₃/Fe₃O₄), thereby enabling in situ formation of the active composite structure. After cooling to room temperature, the resulting nanocomposites were sequentially washed with dilute hydrochloric acid, deionized water, and ethanol to remove residual impurities and loosely bound species. The purified materials were then dried overnight at 80 °C.

The TD-GLC₃-derived nanocomposites were designated as TD-GLC₃@Fe₂O₃/Fe₃O₄@SiO₂-1, TD-GLC₃@Fe₂O₃/Fe₃O₄@SiO₂-2, and TD-GLC₃@Fe₂O₃/Fe₃O₄@SiO₂-3, corresponding to the compositions listed in Table 3.6. The TD-CTrGO₄-derived nanocomposite prepared with the optimal composition was designated TD-CTrGO₄@Fe₂O₃/Fe₃O₄@SiO₂.

For simplicity in subsequent discussion and figure presentation, abbreviated sample codes were adopted as listed in Table 13.

Table 13: Abbreviated sample codes used for nanocomposite materials

Full sample designation	Abbreviated code
TD-GLC ₃ @Fe ₂ O ₃ /Fe ₃ O ₄ @SiO ₂ -1	TGFS-1
TD-GLC ₃ @Fe ₂ O ₃ /Fe ₃ O ₄ @SiO ₂ -2	TGFS-2
TD-GLC ₃ @Fe ₂ O ₃ /Fe ₃ O ₄ @SiO ₂ -3	TGFS-3
TD-CTrGO ₄ @Fe ₂ O ₃ /Fe ₃ O ₄ @SiO ₂	TCGFS

3.8 Material Characterization

The synthesized graphene-like carbon (GLC), graphene oxide (GO), reduced graphene oxide (rGO), doped graphene materials, and graphene-based nanocomposites were characterized using a combination of structural, morphological, compositional, thermal, and electrochemical techniques to evaluate the effects of synthesis, oxidation, reduction, doping, and composite formation on material properties relevant to electrochemical energy storage applications.

Raman spectroscopy was employed extensively throughout the study to evaluate graphitic ordering, structural defects, and disorder within the carbon framework by analyzing the D and G bands and the corresponding (I_D/I_G) ratio. Raman analysis was particularly important for optimization studies involving graphitization, oxidation, and heteroatom doping. Raman measurements for all samples were performed at the Institute Ruđer Bošković (IRB) using a Renishaw InVia spectrometer with a 532 nm laser for GLC optimization study samples, while other samples were analyzed using WITec Alpha300 RA spectrometer.

X-ray diffraction (XRD) analysis was used to investigate crystallinity, the development of graphitic structure, interlayer spacing changes after oxidation, and phase identification in nanocomposite materials containing iron oxides and silica. The technique was also used to assess the influence of thermal treatment and doping on structural ordering. Measurements were conducted at the Faculty of Chemical Engineering and Technology (FCET) at the University of Zagreb, Croatia, using a Shimadzu XRD-6000 powder X-ray diffractometer and at IRB using an ItalStructures APD 2000 X-ray diffractometer.

Morphological characterization was conducted using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM was used to observe surface morphology, porosity development, and particle distribution, while TEM provided insight into nanoscale structural features, graphene sheet morphology, and nanocomposite dispersion. SEM imaging at FCET was performed using a Tescan Vega 3, with EDX analysis using a Bruker XFlash 4010-M detector. Additional SEM/EDX measurements were performed at IRB using a JEOL JSM-7000F FE-SEM coupled with an Oxford Instruments INCA Energy 300 system. TEM measurements were performed in Pakistan using JEOL JEM-2010, 200 *kV*, and AR-STEM; JEOL JEM-ARM200CF, JEOL at the National Chemistry Institute, Slovenia, respectively.

Elemental composition and heteroatom incorporation were evaluated using CHNS elemental analysis, energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). CHNS analysis was primarily used to quantify the incorporation of bulk nitrogen and sulfur during doping studies. At the same time, XPS was applied to selected optimized samples to evaluate surface elemental composition and chemical bonding states. EDX mapping was additionally used to confirm elemental distribution within nanocomposite structures. XPS measurements were performed primarily at the National Centre for Physics (NCP), Islamabad, Pakistan, using a SPECS ProvenX NAP system. For GO reduction and the preliminary residence-time and heating-profile studies, XPS measurements were carried out at the National Chemistry Institute, Slovenia (KI), using a PHI 5000 VersaProbe III (VersaProbe 3 AD system).

Thermogravimetric analysis (TGA) was used to evaluate thermal stability, carbon retention behavior, and oxidation resistance of selected graphene-based materials and doped samples. TGA measurements were performed at FCET using a Mettler Toledo TGA/DSC 3+. Surface area and pore characteristics of selected materials were determined using Brunauer–Emmett–Teller (BET)

surface area analysis. BET measurements were performed at the Interdisciplinary Research Centre in Biomedical Materials (IRCBM), COMSATS University, Pakistan, using a Quantachrome Autosorb iQ2 analyzer, and partly at IRB using a Quantachrome Autosorb iQ3 analyzer.

Due to experimental scope considerations and the prioritization of available instrumental resources across the full experimental matrix, certain characterization techniques were applied selectively based on material availability and sample-quantity requirements. BET surface area analysis was not performed on graphene oxide pathway samples due to the relatively high mass requirement of the available instrumentation (approximately 500 mg per measurement), which was incompatible with the limited yields obtained in early-stage syntheses. TEM and XPS analyses were performed on selected representative samples to provide detailed morphological and surface chemical information.

3.9 Electrochemical Characterization

Electrochemical evaluation of selected graphene-like carbon (GLC), graphene oxide (GO), reduced graphene oxide (rGO), doped graphene materials, and graphene-based nanocomposites was carried out using symmetric two-electrode supercapacitor configurations. Electrochemical testing was performed at specific stages of the study to evaluate the effects of synthesis, oxidation, reduction, doping, and nanocomposite formation on charge storage behavior and electrochemical performance. Electrochemical testing was performed at the Battery Research Center, Faculty of Chemical Engineering and Technology (FCET), University of Zagreb, using a BioLogic VMP-3e multichannel potentiostat. Symmetric supercapacitor cells were assembled using an EL-CELL ECC-REF electrochemical cell, with Figure 6 illustrating the testing setup.

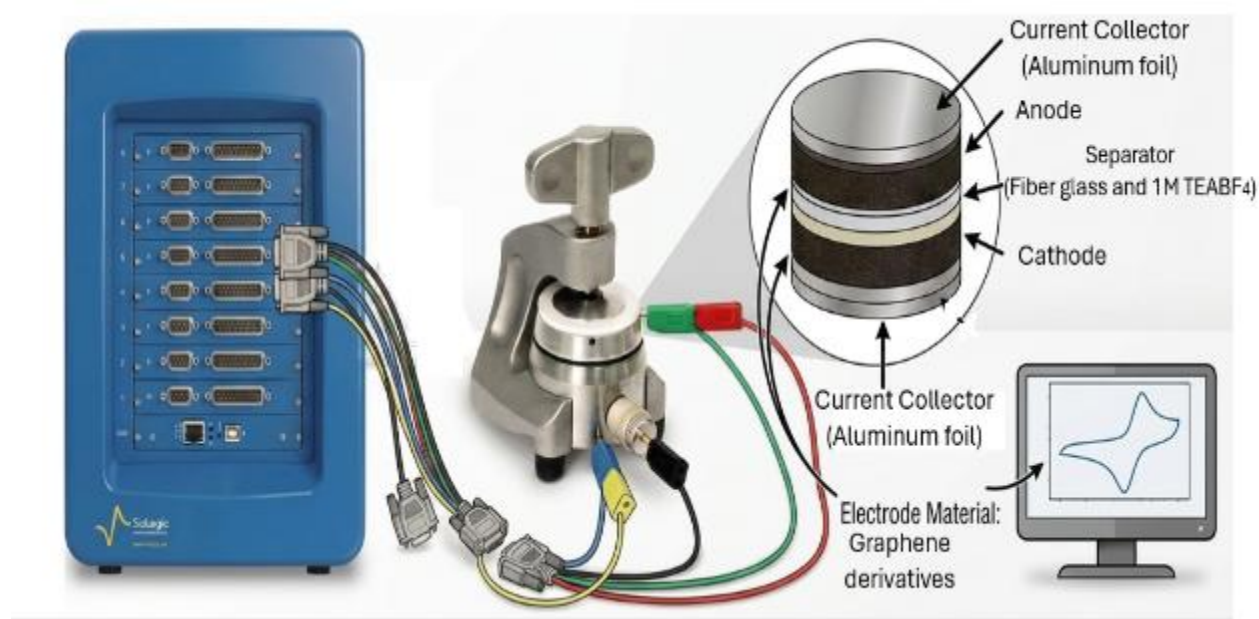


Figure 6. Illustration of the electrochemical measurement setup used in this study.

Since the synthesized materials consistently exhibited characteristics favorable for capacitive energy storage, supercapacitor testing was used throughout the study rather than evaluating lithium-ion batteries.

Working electrodes were prepared by dispersing the active material, carbon black, and polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP) at an 8:1:1 mass ratio. The slurry was homogenized and coated onto aluminum foil current collectors using the doctor-blade technique, then dried under vacuum at 60 °C. The mass loading of active material was approximately 1.0 mg cm⁻². Circular electrodes with a diameter of 18 mm were assembled into symmetric coin-type cells using an EL-CELL configuration with glass fiber separators.

Electrochemical measurements were conducted using 1.0 M tetraethylammonium tetrafluoroborate in acetonitrile (TEABF₄/ACN) as the electrolyte. Cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS)

measurements were performed to evaluate capacitive behavior, charge–discharge characteristics, resistance, and ion transport properties.

Cyclic voltammetry measurements were typically conducted over the 0–3.0 V voltage window at a scan rate of 20 mV s⁻¹. Galvanostatic charge–discharge measurements were performed over a practical operating voltage range of 1.0–3.0 V at current densities that varied with the experimental stage and material under investigation. Short-term cycling stability and early electrochemical behavior were additionally evaluated by performing repeated GCD cycling over 100 charge–discharge cycles.

Electrochemical impedance spectroscopy measurements were recorded over a frequency range of 200 kHz to 10 mHz using a 10 mV AC perturbation at open-circuit potential. The resulting Nyquist plots were used to evaluate the equivalent series resistance, charge-transfer resistance, ion-diffusion characteristics, and capacitive behavior of the assembled devices.

The specific capacitance from cyclic voltammetry was calculated according to Equation (1):

$$C_{sp} = \frac{\int I(V) dV}{2 m \nu \Delta V} \quad (1)$$

where (C_{sp}) is the specific capacitance (F g⁻¹), ($\int I(V) dV$) is the integrated area under the CV curve, (m) is the total mass of active material in both electrodes (g), (ν) is the scan rate (V s⁻¹), and (ΔV) is the operating voltage window (V).

The specific capacitance from galvanostatic charge–discharge measurements was calculated using Equation (2):

$$C_{sp} = \frac{4I\Delta V}{m\Delta t} \quad (2)$$

where (I) is the discharge current (A), (Δt) is the discharge time (s), (m) is the total mass of active material in both electrodes (g), and (ΔV) is the discharge voltage window excluding the IR drop.

The specific energy density (E) and specific power density (P) were calculated using Equations (3) and (4), respectively:

$$E \text{ (Wh kg}^{-1}\text{)} = (1/2) \times C_{\text{device}} \times V^2 \times (1000/3600) \quad (3)$$

$$P \text{ (W kg}^{-1}\text{)} = (E / \Delta t) \times 3600 \quad (4)$$

where (C_{device}) is the full-device specific capacitance obtained from the discharge curve, (V) is the practical operating voltage window, and (Δt) is the discharge time. In this study, a stable working voltage window of 2.0 V was typically employed, corresponding to charging up to 3.0 V and discharging to 1.0 V.

Equivalent series resistance (ESR) values were estimated from the instantaneous IR drop observed during galvanostatic discharge curves. Electrochemical measurements were primarily intended to establish correlations among material synthesis, structural evolution, and capacitive performance, rather than to achieve comprehensive optimization of commercial devices.

Methodological Hierarchy and Experimental Logic

The experimental design adopted in this study follows a hierarchical and staged framework rather than a single-route optimization strategy. The overall methodology is structured into sequential phases: preliminary screening experiments, baseline definition, statistical optimization, and application-oriented synthesis.

Preliminary experiments were used to evaluate the influence of key processing variables and to define stable, reproducible baseline conditions for each synthesis route. These experiments were not intended for optimization but served to reduce process uncertainty before statistical design.

Subsequently, the Taguchi method, combined with Grey Relational Analysis, was applied within the defined system boundaries to optimize selected controllable synthesis parameters. This stage was conducted under fixed baseline conditions to ensure statistical validity and isolate the effects of individual factors. The optimized parameter sets obtained from statistical analysis represent locally optimal conditions within each defined system. However, their implementation in later stages was additionally guided by practical considerations such as scalability, precursor availability, and process stability, ensuring compatibility with extended synthesis routes.

Across the study, material development proceeds through interconnected but functionally distinct pathways, including graphene-like carbon formation, graphene oxide synthesis, reduction, doping, and nanocomposite fabrication. Each pathway was optimized or refined within its own experimental scope, rather than forced into a single unified parameter set.

This hierarchical approach ensures that all experimental decisions are traceable to either screening logic, statistical optimization, or practical implementation constraints. As a result, variations in catalyst selection, activation conditions, and thermal profiles reflect stage-specific requirements rather than methodological inconsistency.

Overall, the methodology is therefore best interpreted as a staged optimization framework with constrained decision transfer between phases, enabling both systematic parameter optimization and flexible material development.

4. RESULTS AND DISCUSSION

4.1 Graphene-Like Carbon (GLC) Synthesized via Simultaneous Chemical Activation and Catalytic Graphitization

4.1.1 Preliminary Evaluation of Thermal Residence Profiles

The different thermal residence profiles produced GLC materials with noticeable variations in their structural development, surface chemistry, morphology, and electrochemical response. These differences indicate how the heating history influences the balance between carbon activation, graphitization, and the final material properties [48]. The results from the different residence profiles are discussed below in terms of these changes and their relationship to the observed material characteristics. Particular attention is given to how the thermal treatment affected the structure and properties of the resulting GLC materials.

4.1.1.1 Structural, functional, and morphological characterization

As stated in the methodology, the synthesized samples from this preliminary investigation were analyzed using various analytical methods, with structural analysis (Raman and XRD) as the first. Since the three samples were prepared from the same biochar precursor with identical KOH and Fe loadings, the differences observed in the Raman and XRD analyses (Figure 7) can be primarily attributed to the thermal residence profile that was employed during pyrolysis. The results indicate that the timing and duration of intermediate dwell stages strongly influence the balance between KOH activation and Fe-catalyzed graphitization [24, 49].

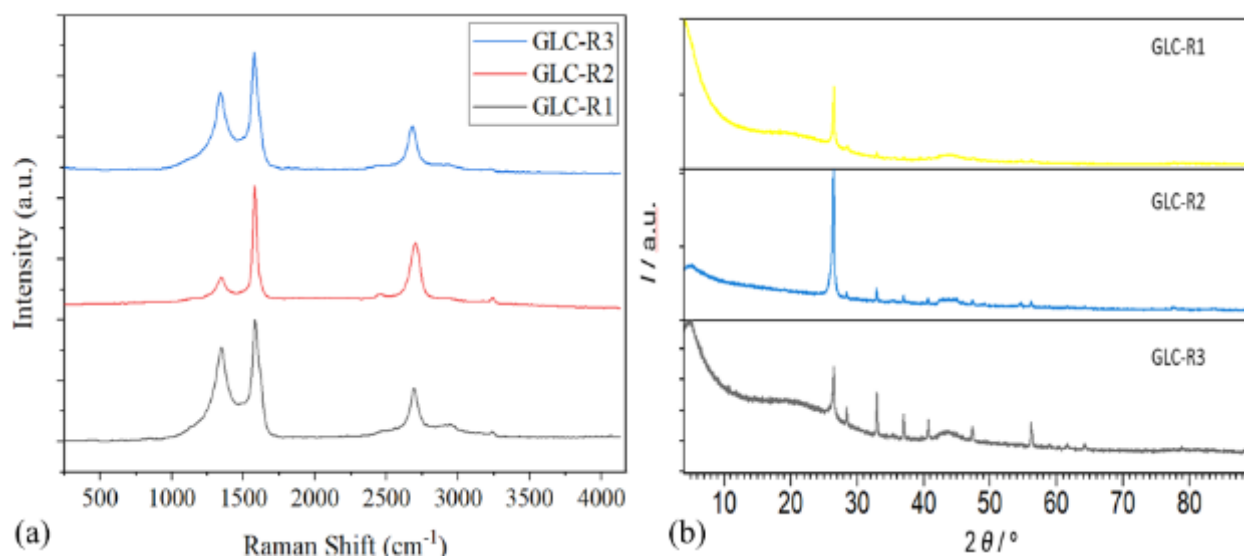


Figure 7. Structural characterization of GLC-R1, GLC-R2, and GLC-R3 using (a) Raman spectroscopy and (b) X-ray diffraction (XRD).

Looking at the structural data in Table 14, GLC-R2 stood out as the most well-ordered material of the three. It had the lowest I_D/I_G ratio (0.24), the highest I_{2D}/I_G value (0.52), and the largest crystallite size, with L_a reaching 80.10 nm. The Raman findings matched up with the XRD results: GLC-R2 showed a strong and sharp (002) peak at around 26.4° , which points to highly ordered graphitic regions and a smaller number of few-layer graphene-like structures [26, 105]. This high degree of order probably comes from including a 400°C dwell stage, which gives KOH time to move into the biochar and helping iron catalysts form before the temperature ramps up to 900°C for graphitization [17, 30].

Table 14. Raman structural parameters of GLC samples prepared using different thermal residence profiles.

Sample	I_D/I_G Ratio	I_{2D}/I_G Ratio	L_a Grain Size (nm)
GLC-R1	0.77	0.44	24.97
GLC-R2	0.24	0.52	80.10
GLC-R3	0.66	0.39	29.13

GLC-R1 followed a different pathway. Direct heating to 900 °C subjected the material to simultaneous activation and graphitization, resulting in a higher defect density ($I_D/I_G = 0.77$) and smaller crystallite size ($L_a = 24.97$ nm). Despite this, GLC-R1 exhibited the second most intense (002) reflection, suggesting that the extended 90 min residence at 900 °C promoted graphitic stacking even as aggressive KOH activation generated defects. This indicates that graphitic ordering and defect formation can occur concurrently during catalytic graphitization [26]. Looking at the results for GLC-R3, it's clear that adding too many intermediate heating steps can have drawbacks. Even though the sample went through an extra heating stage at 800 °C, it ended up less ordered than GLC-R2. The I_D/I_G ratio was higher at 0.66, and the crystallite size (L_a) was smaller at 29.13 nm. Spending too much time at lower temperatures seems to have disrupted the structure more, while the brief 30-minute heating at 900 °C did not allow enough time for the material to reorganize into well-ordered graphite. This is why GLC-R3 showed a weaker (002) peak and signs of other crystalline phases forming.

To further support the structural differences observed from the Raman and XRD analyses (Figure 5a-b), the thermal stability, surface chemistry, and morphology of the GLC materials were examined using TGA, FTIR, and FE-SEM/EDS (Figures 8 and 9).

The TGA curves shown in Figure 6a reveal noticeable differences in thermal stability between the samples. GLC-R1 experienced the highest mass loss, losing approximately 21% of its weight by 800 °C, whereas GLC-R2 and GLC-R3 lost only about 7% and 4%, respectively. The greater mass loss observed for GLC-R1 suggests that a larger fraction of unstable carbon species and residual oxygen-containing groups remained after pyrolysis. This behavior is consistent with the Raman results, in which GLC-R1 exhibited the highest defect level among the samples. In contrast, the lower weight losses observed for GLC-R2 and GLC-R3 indicate that GLC-R1's aggressive thermal

profile contributed to its higher mass loss. However, despite its lower overall mass loss, GLC-R3 did not exhibit the same level of structural ordering as GLC-R2, indicating that thermal stability and graphitic ordering do not necessarily develop to the same extent.

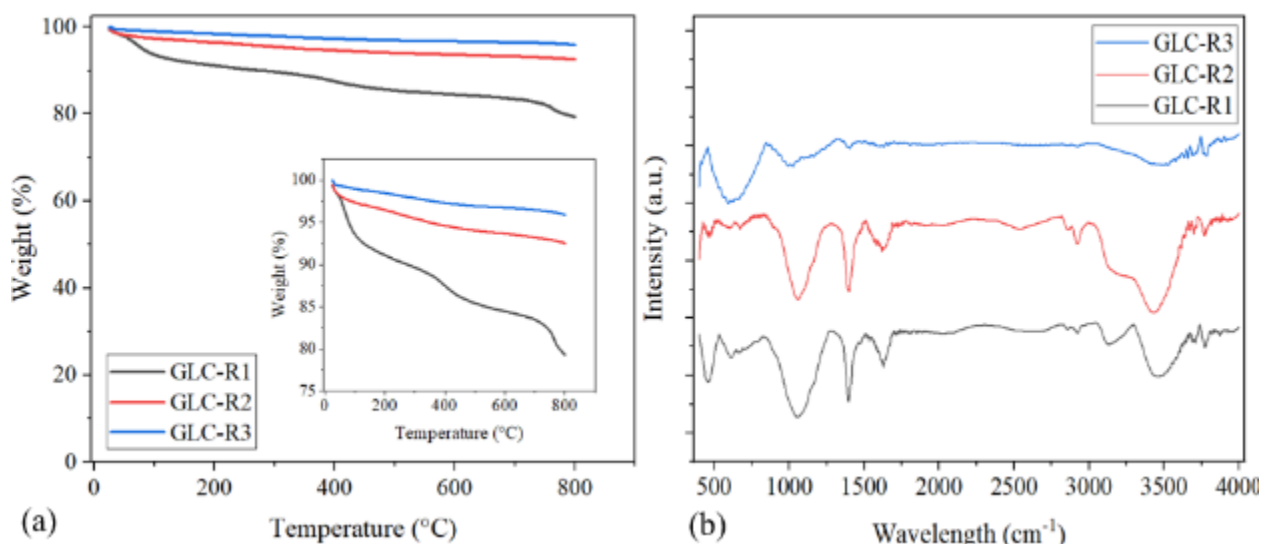


Figure 8. TGA (a) and FTIR (b) analysis of GLC-R1, GLC-R2, and GLC-R3 prepared using different thermal residence profiles.

The combined FTIR spectra shown in Figure 8b show noticeable differences among the samples. While GLC-R1 displayed a broad O–H stretching band around 3450 cm^{-1} and a pronounced C–O vibration near 1050 cm^{-1} [18, 63], both indicating the presence of residual oxygen-containing groups, in GLC-R2 these signals were weak, denoting more complete removal of surface oxygen functionalities during thermal treatment [69]. GLC-R3 also exhibits weaker oxygen-related bands, indicating significant deoxygenation during the longer dwell stages. The Raman and XRD results indicate that this additional thermal exposure has a stronger impact on volatile elimination than on increasing the degree of graphitic ordering [40].

The FE-SEM micrographs (Figure 9a, c and e) reveal that all three samples developed porous carbon structures as a result of KOH activation [15, 106]. However, clear differences in the carbon

framework are evident. GLC-R1 exhibited a more fragmented and irregular morphology, consistent with the aggressive activation conditions associated with direct heating to 900 °C [105, 107]. In contrast, GLC-R2 displayed a more continuous carbon framework with well-developed pore structures, suggesting that the intermediate 400 °C dwell allowed activation and graphitization to proceed in a more controlled manner. Although GLC-R3 retained a porous structure, its morphology appeared less uniform than that of GLC-R2, showing the increased structural disorder observed from Raman analysis.

The elemental compositions of the samples, derived from EDS (Figure 9b, d, and f), reflect a consistent trend among them. GLC-R1 contained 93.42 wt% carbon and 6.18 wt% oxygen. The data show that GLC-R2 exhibited the highest carbon content (96.30 wt%) and the lowest oxygen content (3.18 wt%). GLC-R3 showed intermediate values with 95.63 wt% carbon and 4.13 wt% oxygen. While direct heating of GLC-R1 led to a more aggressive process and higher oxygen content, the 400 °C dwell stage in GLC-R2 appeared remarkably effective at promoting deoxygenation and retaining the carbon framework's integrity. Small residual amounts of potassium (0.79 wt%) in GLC-R2 and chlorine (0.23 wt%) in GLC-R3 were also present, originating from the activation and catalyst precursor stages.

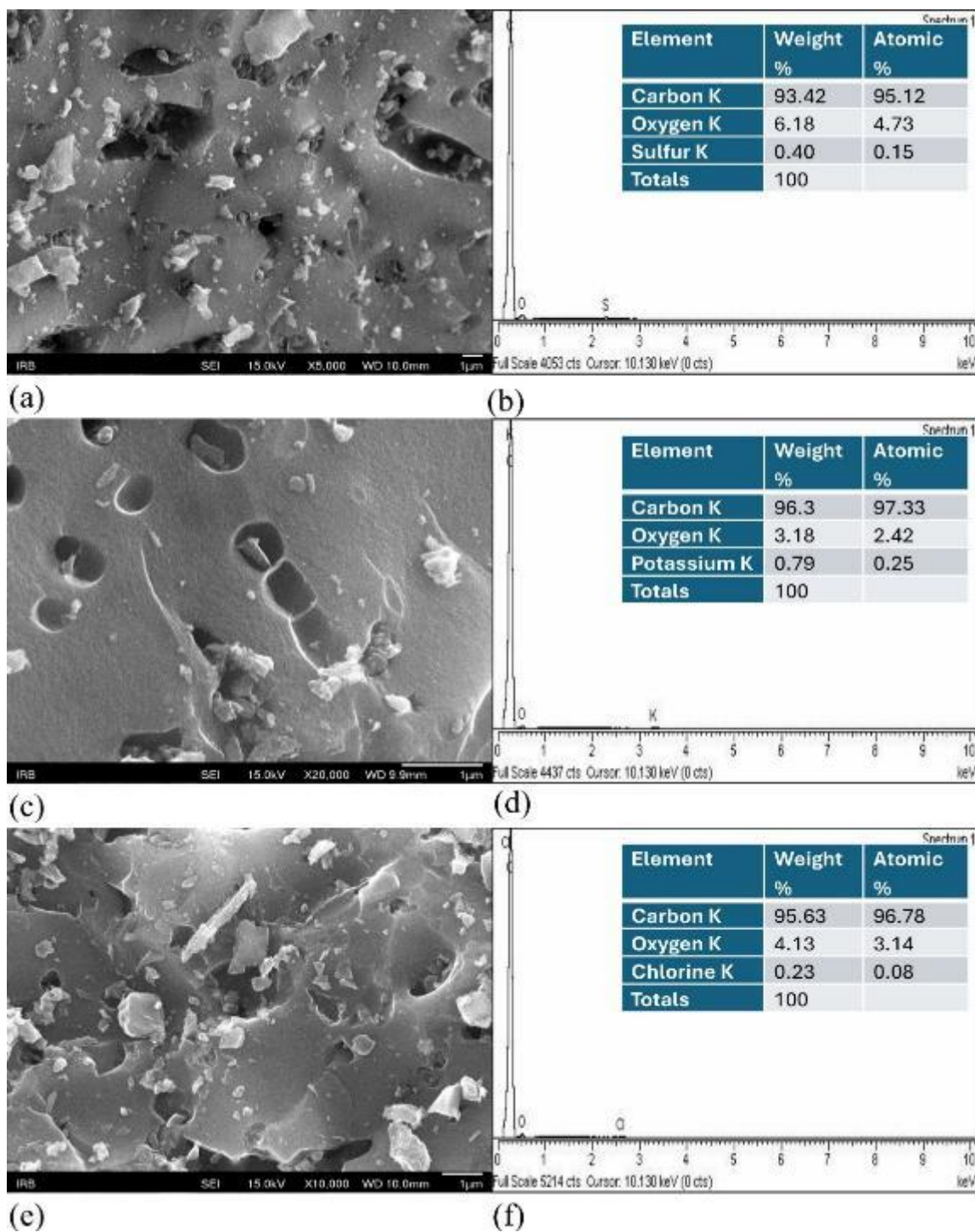


Figure 9. Morphological and elemental characterization of GLC-R1, GLC-R2, and GLC-R3 using (a, c, e) SEM images and (b, d, f) corresponding EDX spectra.

The TGA, FTIR, FE-SEM, and EDS findings echo the structural conclusions reached with Raman spectroscopy and XRD. All three thermal profiles produced porous graphene-like carbon

materials, but the GLC-R2 residence profile stands out for achieving the most effective balance between activation and graphitization. This condition led to greater structural order, lower oxygen content, enhanced thermal stability, and a more uniform carbon framework.

4.1.1.2. Electrochemical performance of glc materials in supercapacitor applications

Figure 10 shows the curves generated for CV, GCD, and EIS analysis of the 3 samples. Despite exhibiting the highest degree of graphitic ordering, GLC-R2 did not deliver the best electrochemical performance in the organic electrolyte system (Figure 8). Instead, GLC-R1 produced the highest specific capacitance, reaching 68.0 F g^{-1} from CV and 71.34 F g^{-1} from GCD, compared with 42.67 and 41.00 F g^{-1} for GLC-R2, respectively. GLC-R3 showed intermediate behavior, achieving a GCD capacitance of 63.06 F g^{-1} despite its comparatively disordered structure.

The electrochemical analysis results indicate that maximizing graphitic order alone does not necessarily maximize charge storage [7, 53, 54]. From Table 15, while GLC-R2 exhibited the lowest ESR (2.05Ω), its highly ordered carbon framework likely contained fewer defect sites and a lower accessible surface area for ion adsorption. In contrast, GLC-R1 retained a greater degree of structural defects, as suggested by its higher I_D/I_G ratio, but at the same time, it maintained substantial graphitic character through its pronounced (002) reflection. This combination provides a more favourable balance between electrical conductivity and electrochemically accessible surface area, resulting in improved capacitance. The attribute is particularly relevant in TEABF₄/ACN electrolytes, where the relatively large solvated ions require a pore structure that is easily accessible and electrically conductive [56].

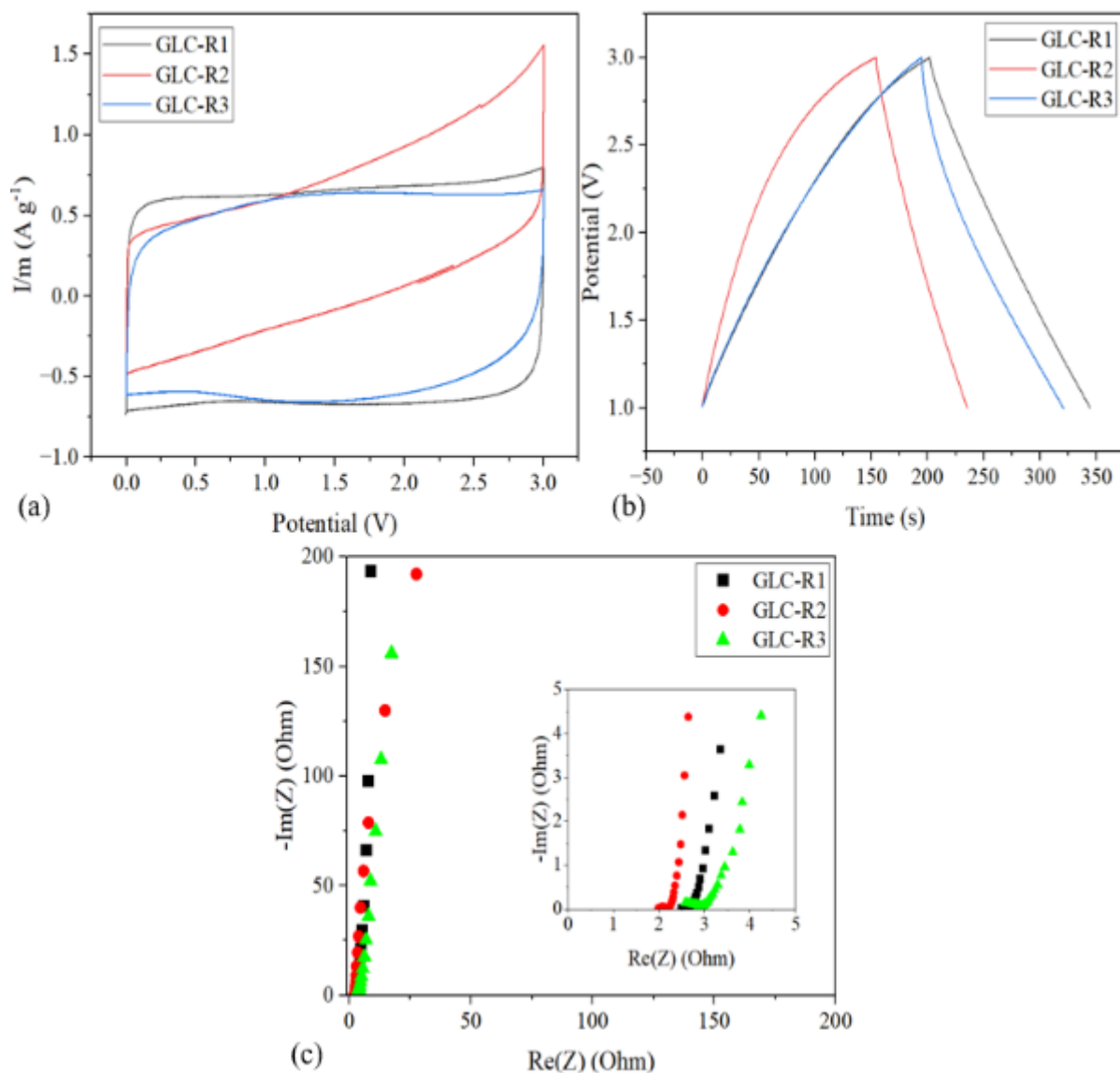


Figure 10. Electrochemical characterization of GLC-R1, GLC-R2, and GLC-R3 using (a) cyclic voltammetry (CV), (b) galvanostatic charge–discharge (GCD), and (c) electrochemical impedance spectroscopy (EIS).

When graphitization is excessive, it may improve charge transport but can simultaneously reduce the number of active adsorption sites available for charge storage [20, 108]. Similar balances between graphitic ordering and capacitance have been widely reported for activated graphene-like carbons and porous graphitic carbons used in organic electrolyte supercapacitors [4, 5, 7].

Table 15. Electrochemical performance parameters of GLC-R1, GLC-R2, and GLC-R3 measured in TEABF₄/acetonitrile electrolyte.

Sample	CV (C _s / F g ⁻¹)	GCD (C _s / F g ⁻¹)	ESR (Ω)
GLC-R1	68.00	71.34	2.31
GLC-R2	42.67	41.00	2.05
GLC-R3	64.00	63.06	2.57

Overall, the electrochemical results suggest that the optimum material is not necessarily the most ordered one. Instead, performance depends on achieving a balance between conductivity and defect-derived surface accessibility. From this perspective, GLC-R1 thermal condition provided the most favourable combination of properties and was therefore selected for subsequent optimization.

Selection of Thermal Treatment Strategy for Further Optimization

The comparison of the three thermal profiles revealed that improved structural ordering does not necessarily translate into superior electrochemical performance. As observed, GLC-R2 developed the most ordered graphitic framework and the highest thermal stability, but GLC-R1 delivered the highest capacitance. This suggests that a balance between graphitic domains, defects, and accessible active sites is more important than structural order alone. In addition, the single-step heating approach used for GLC-R1 provided a simpler and more reproducible synthesis route compared with the multi-stage profiles, which introduced additional processing complexity without clear electrochemical advantages.

Therefore, GLC-R1 was selected as the starting condition for subsequent optimization of the synthesis parameters. This selection represents a practical screening decision rather than the confirmation of an optimum thermal profile. A more controlled approach through systematic optimization of the synthesis method is required to determine whether adjustments to the activation

and graphitization conditions can improve the balance between structural development and electrochemical performance.

4.1.2 Optimization of Synthesis Parameters on Graphene-like Carbon Formation

This section presents the optimization of the GLC synthesis parameters using the L9 experimental design approach. The influence of the selected process variables is evaluated based on the measured responses, followed by analysis of their effects on the structural characteristics and electrochemical performance of the resulting materials. The results presented here are predominantly based on the author's recently published work [104], which forms part of the present dissertation.

4.1.2.1 Response variability across the L9 experimental matrix

L9 of the Taguchi orthogonal array described in the methodology was used to evaluate the influence of synthesis parameters on the formation of graphene-like carbon. Considerable variation was observed across the experimental matrix, indicating strong dependence of the final material properties on activation intensity, catalyst loading, particle size, and pyrolysis temperature [109, 110]. The differences between the experimental runs were reflected across the measured responses, showing that changes in the synthesis conditions produced distinct material characteristics. This variation provided a basis for comparing the individual runs and identifying the conditions associated with the desired GLC properties. The measured responses for all experimental runs are summarized in Table 16, while representative TGA curves, Raman spectra, and nitrogen adsorption–desorption isotherms are presented in Figure 11.

Table 16: L9 orthogonal array experimental design and measured responses for synthesized graphene-like carbon samples

Particle size (μm)	KOH:Biochar ratio (w/w)	Ferrocene dose (%)	Temperature ($^{\circ}\text{C}$)	Yield (g)	BET surface area (m^2g^{-1})	I_D/I_G (N/A)	TGA mass retention (%)
97	1	15	1000	4.70	32	0.81	81
125	2	10	1000	3.15	369.4	0.8	85
75	2	15	900	3.80	619.5	0.95	86
97	2	20	800	4.20	276.2	1.00	84
75	1	10	800	4.01	73	0.92	79
97	3	10	900	2.88	1217.2	0.3	92
125	3	15	800	3.37	929.4	0.43	91
75	3	20	1000	3.50	559.1	0.81	95
125	1	20	900	4.85	62	0.91	87

The results indicate a distinct trade-off between porosity development and synthesis yield. Samples subjected to more aggressive activation conditions generally exhibited significantly higher BET surface areas but lower recovered mass, attributable to intensified carbon consumption during pyrolysis [111-115]. This trend was most pronounced in Run 6, which achieved the highest BET surface area ($1217.2 \text{ m}^2 \text{ g}^{-1}$) but the lowest synthesis yield (2.88 g). In contrast, Run 9 yielded the highest mass (4.85 g) but demonstrated limited pore development, with a BET surface area of only $62 \text{ m}^2 \text{ g}^{-1}$.

Thermal stability analysis indicated that all samples remained stable at elevated temperatures under all investigated conditions, with TGA mass retention values ranging from 79% to 95% at 800°C . This narrow range in thermal retention suggests that each synthesis condition produced structurally stable carbon frameworks, despite substantial differences in pore development and graphitic ordering [26, 41].

The Raman spectra shown in Figure 9b revealed substantial differences in structural disorder among the synthesized materials. Variations in the I_D/I_G ratio indicate that synthesis conditions strongly influenced the extent of graphitic reconstruction during pyrolysis [16, 40, 112]. Lower I_D/I_G values were generally associated with improved structural ordering and more effective catalytic graphitization [16, 26, 116].

The nitrogen adsorption–desorption isotherms shown in Figure 9c, similar to the Raman spectra, demonstrate substantial differences in adsorption behavior and pore evolution across the experimental runs. These observations confirm that activation intensity and thermal treatment exerted a dominant influence on the development of hierarchical porous carbon architectures [15, 117].

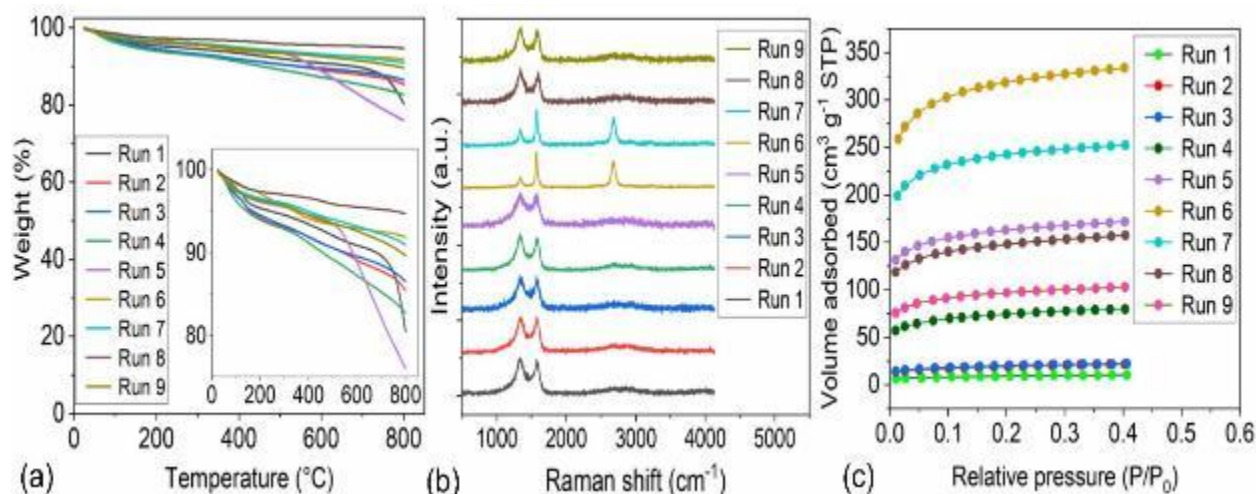


Figure 11. (a) TGA curves, (b) Raman spectra, and (c) nitrogen adsorption–desorption isotherms of GLC samples obtained from the nine experimental conditions in the Taguchi design [104].

4.1.2.2 Multi-Response Optimization Using Grey Relational Analysis

Because no single experimental run simultaneously maximized all measured responses, Grey Relational Analysis (GRA) was employed to identify the optimum synthesis condition based on overall material performance [118]. The grey relational grade (GRG) was used as an integrated

performance index combining synthesis yield, BET surface area, Raman I_D/I_G ratio, and TGA mass retention [118]. The normalized response values, grey relational coefficients, and detailed GRG calculations are presented in the supplementary part of this dissertation.

The calculated GRG values for the nine experimental runs are ranked and displayed in Figure 12a. Among all the conditions investigated, Run 6 achieved the highest GRG value of 0.882, indicating the best overall multi-response performance within the experimental design space. In contrast, Run 1 produced the lowest GRG value (0.404), reflecting comparatively limited overall performance despite acceptable synthesis yield.

The optimum synthesis condition identified through the Taguchi–GRA framework corresponded to:

- Particle size: 97 μm (A2)
- KOH:Biochar ratio: 3:1 (B3)
- Ferrocene dosage: 10% (C1)
- Pyrolysis temperature: 900 $^{\circ}\text{C}$ (D2)

To evaluate the reliability of the optimization process, a sensitivity analysis was performed using alternative weighting schemes that emphasized either BET surface area or structural ordering. As shown in Figure 12b. Run 6 consistently ranked highest across all weighting configurations, confirming the robustness of the identified optimal parameter set [118]. The main effects plots in Figure 12c illustrate the influence of individual factor levels on optimization performance. The results indicate that optimal performance was associated with an intermediate particle size, high

KOH loading, a relatively low catalyst dosage, and a moderate pyrolysis temperature [15, 42, 106, 119].

In summary, the GRA approach facilitated the simultaneous optimization of competing synthesis responses using a single integrated performance index [118].

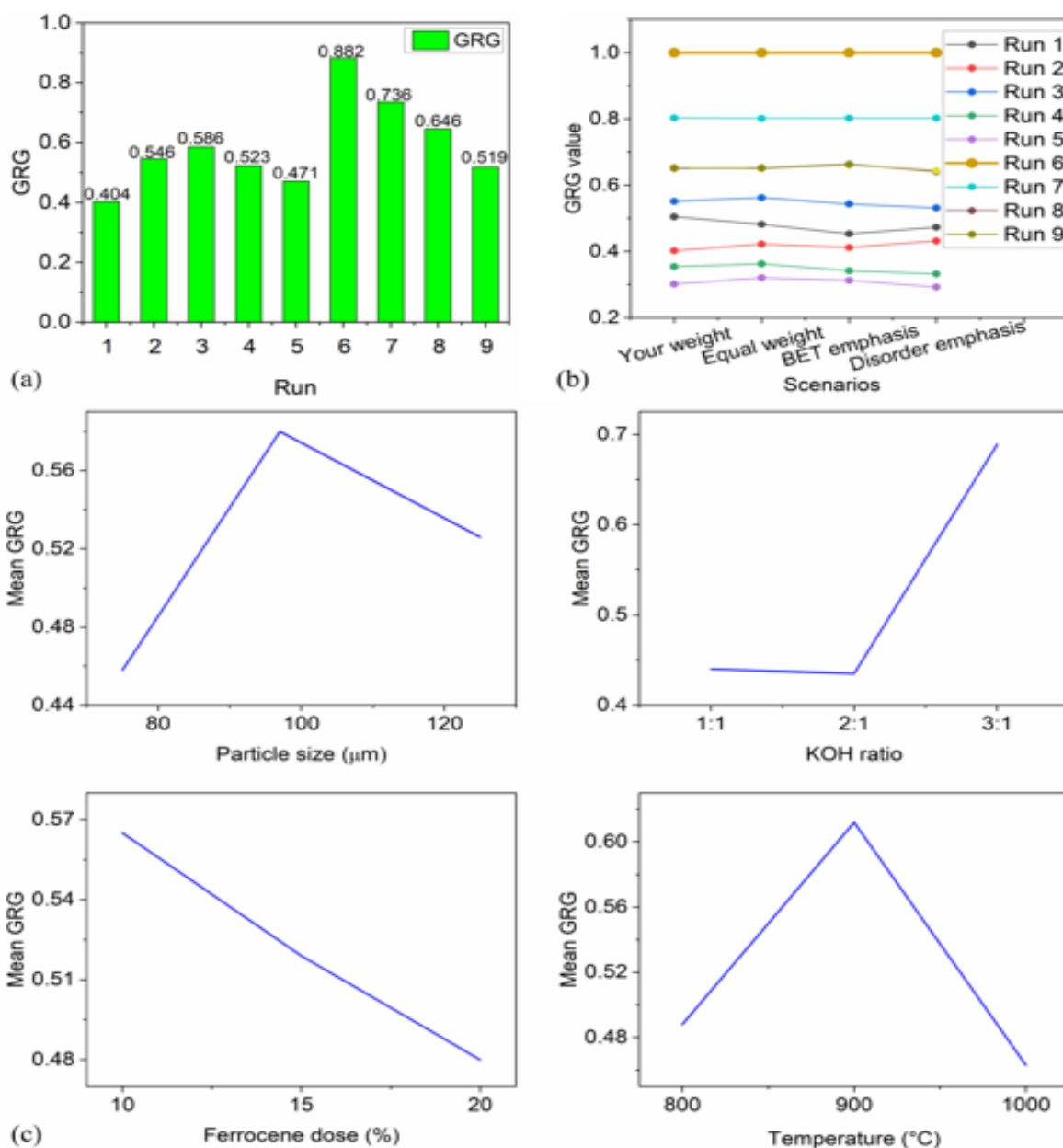


Figure 12. Summary of the Taguchi–grey relational optimization, showing (a) main effects plots for the mean grey relational grade, (b) weighting sensitivity analysis for the optimal synthesis condition, and (c) grey relational grade rankings across all experimental runs [104].

4.1.2.3 Effect of Individual Synthesis Parameters

The main effects analysis revealed that all investigated synthesis parameters influenced graphene-like carbon formation, although their relative contributions differed substantially.

The KOH-to-biochar ratio exhibited the strongest influence on overall material performance. Increasing the activation ratio from 1:1 to 3:1 significantly enhanced BET surface area and improved structural ordering, although at the expense of synthesis yield. The increased activation intensity promoted more extensive pore generation and carbon etching during pyrolysis [42, 106, 114, 115, 117].

Pyrolysis temperature also strongly affected material development. The intermediate temperature of 900 °C produced the best overall performance, whereas 800 °C was insufficient for effective catalytic restructuring, and 1000 °C resulted in excessive carbon consumption and partial loss of structural integrity. The superior performance observed at 900 °C suggests that this temperature provided a favorable balance between graphitic reconstruction and pore preservation [16, 112, 116, 120].

Ferrocene dosage showed an inverse relationship with optimization performance. The lowest catalyst dosage (10%) produced the highest mean GRG, indicating that relatively low catalyst loading was sufficient to promote structural ordering. Increasing catalyst concentration beyond this level did not improve overall performance and may have contributed to catalyst agglomeration or excessive catalytic gasification [23, 28, 121].

Particle size also influenced synthesis behavior. The intermediate particle size of 97 µm produced the highest overall performance, likely due to improved balance between reagent accessibility and

structural stability. Larger particles may have limited penetration by the activating agent, whereas smaller particles are more susceptible to excessive activation [106, 113].

Collectively, these results indicate that graphene-like carbon formation was highly dependent on achieving an appropriate balance between chemical activation and catalytic graphitization within the integrated one-step synthesis strategy [16, 42, 106, 112, 116, 120].

4.1.2.4 Statistical Evaluation by ANOVA

Analysis of variance (ANOVA) was performed to evaluate the statistical contribution of the investigated synthesis parameters to the measured responses. The ANOVA outputs for synthesis yield, BET surface area, Raman I_D/I_G ratio, and TGA mass retention are presented in Appendix A Table A1.

ANOVA identified the KOH-to-biochar ratio as the most statistically influential parameter affecting BET surface area, Raman I_D/I_G ratio, and synthesis yield within the investigated design space. This confirms the dominant role of activation intensity in controlling both pore evolution and structural development during graphene-like carbon synthesis.

Pyrolysis temperature and ferrocene dosage also contributed to graphitic ordering and thermal stability, although their statistical influence was comparatively lower within the resolution of the L9 orthogonal array design. Particle size made a more moderate contribution but still influenced the overall optimization behavior through its effects on diffusion and activation uniformity.

The ANOVA results support the trends identified by Grey Relational Analysis and confirm that the optimization of graphene-like carbon synthesis is primarily governed by the interaction between activation intensity and catalytic restructuring behavior.

4.1.2.5 Selection of the Optimized GLC Sample

Based on the combined Taguchi–GRA optimization results, Run 6 was selected as the optimum synthesis condition and designated as GLC-OPT. The optimized synthesis parameters consisted of a biochar particle size of 97 μm , a KOH-to-biochar ratio of 3:1, a ferrocene dosage of 10%, and a pyrolysis temperature of 900 $^{\circ}\text{C}$.

Under these conditions, the synthesized material achieved a BET surface area of 1217.2 $\text{m}^2 \text{g}^{-1}$, a Raman $I_{\text{D}}/I_{\text{G}}$ ratio of 0.30, and a TGA mass retention of 92%, indicating the successful formation of a hierarchically porous and structurally ordered carbon framework.

The subsequent sections discuss the structural, morphological, and electrochemical characteristics of GLC-OPT.

4.1.3 Structural and Morphological Characteristics of Optimized GLC

The optimized graphene-like carbon sample (GLC-OPT) exhibited substantial graphitic ordering while maintaining a highly porous carbon framework, indicating successful integration of chemical activation and catalytic graphitization within a single synthesis process. Structural and compositional characterization results are summarized in Figure 13.

The XRD pattern shown in Figure 13a displayed a broad but distinguishable (002) reflection centered at $2\theta \approx 25.89^{\circ}$, corresponding to an interlayer spacing (d_{002}) of approximately 0.3439 nm. Although larger than that of crystalline graphite, this spacing is characteristic of turbostratic graphitic carbon structures commonly observed in biomass-derived graphene-like materials [105, 122]. The calculated crystallite dimensions further suggest the formation of partially ordered graphitic domains rather than fully amorphous carbon [123].

The Raman spectrum presented in Figure 13b exhibited the characteristic D, G, and 2D bands associated with graphitic carbon materials. The relatively low I_D/I_G ratio of 0.30 confirmed substantial reduction in structural disorder following catalytic graphitization [40]. The appearance of a distinct 2D band further supports the formation of graphene-like stacked domains within the carbon framework [16, 40].

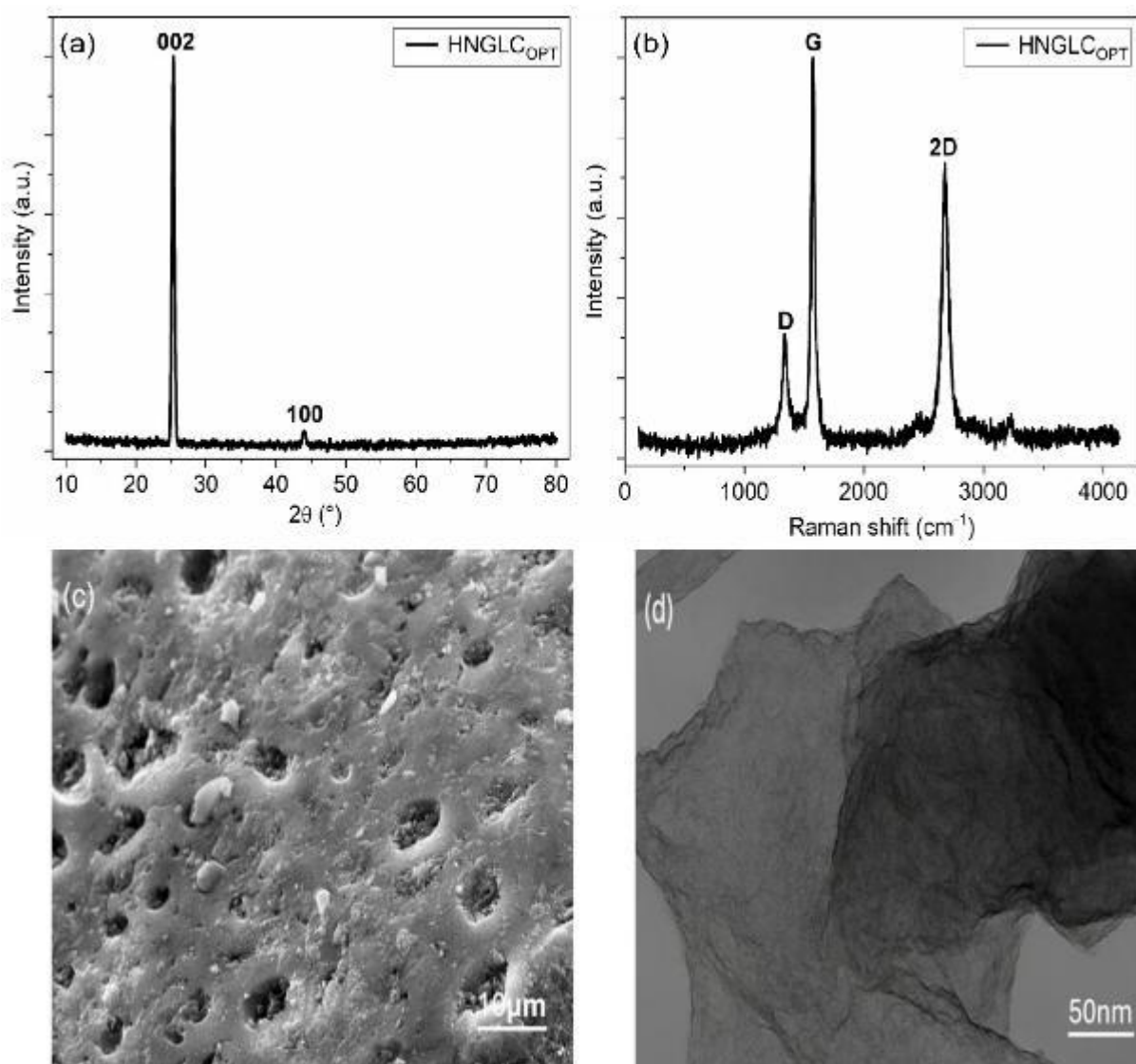


Figure 13. Multiscale structural and morphological characterization of GLC-OPT, including (a) the XRD pattern, (b) Raman spectrum, (c) SEM micrograph, and (d) HRTEM image.

The combined XRD and Raman results confirm substantial structural reorganization of the precursor carbon during pyrolysis. The observed ordering behavior is attributed to catalytic restructuring induced by iron nanoparticles generated from ferrocene decomposition [16, 23, 116, 120].

SEM analysis, shown in Figure 13c, revealed an interconnected porous morphology with irregular cavities and rough carbon surfaces characteristic of chemically activated carbon materials. The observed framework reflects extensive pore development generated during KOH activation [117].

At higher magnification, the HRTEM image shown in Figure 13d revealed partially stacked and curved graphitic layers distributed throughout the porous structure. Localized lattice fringes corresponding to graphitic domains were also observed, supporting the occurrence of catalytic graphitization during thermal treatment.

Elemental composition and surface chemistry were further evaluated using EDX and XPS analyses. The EDX spectrum shown in Figure 14 confirmed that the optimized material consisted predominantly of carbon, with only trace residual inorganic species remaining after post-treatment purification. Minimal residual iron and potassium signals indicate effective removal of catalyst and activating-agent residues.

The XPS C1s spectrum shown in Figure 14a was dominated by sp^2 -bonded carbon centered near 285 eV, confirming the graphitic character of the synthesized material. Minor oxygen-containing surface functionalities associated with C–O and C=O bonding were also detected.

Nitrogen adsorption–desorption analysis further confirmed the hierarchical pore architecture of GLC-OPT. The isotherm shown in Figure 14c exhibited combined Type I and Type IV characteristics with an H4 hysteresis loop, indicating the coexistence of microporous and

mesoporous structures [124]. Pore size distribution analysis revealed a dominant micropore population near 1 nm, along with broader mesoporous channels that may facilitate electrolyte transport and ion diffusion [117, 125].

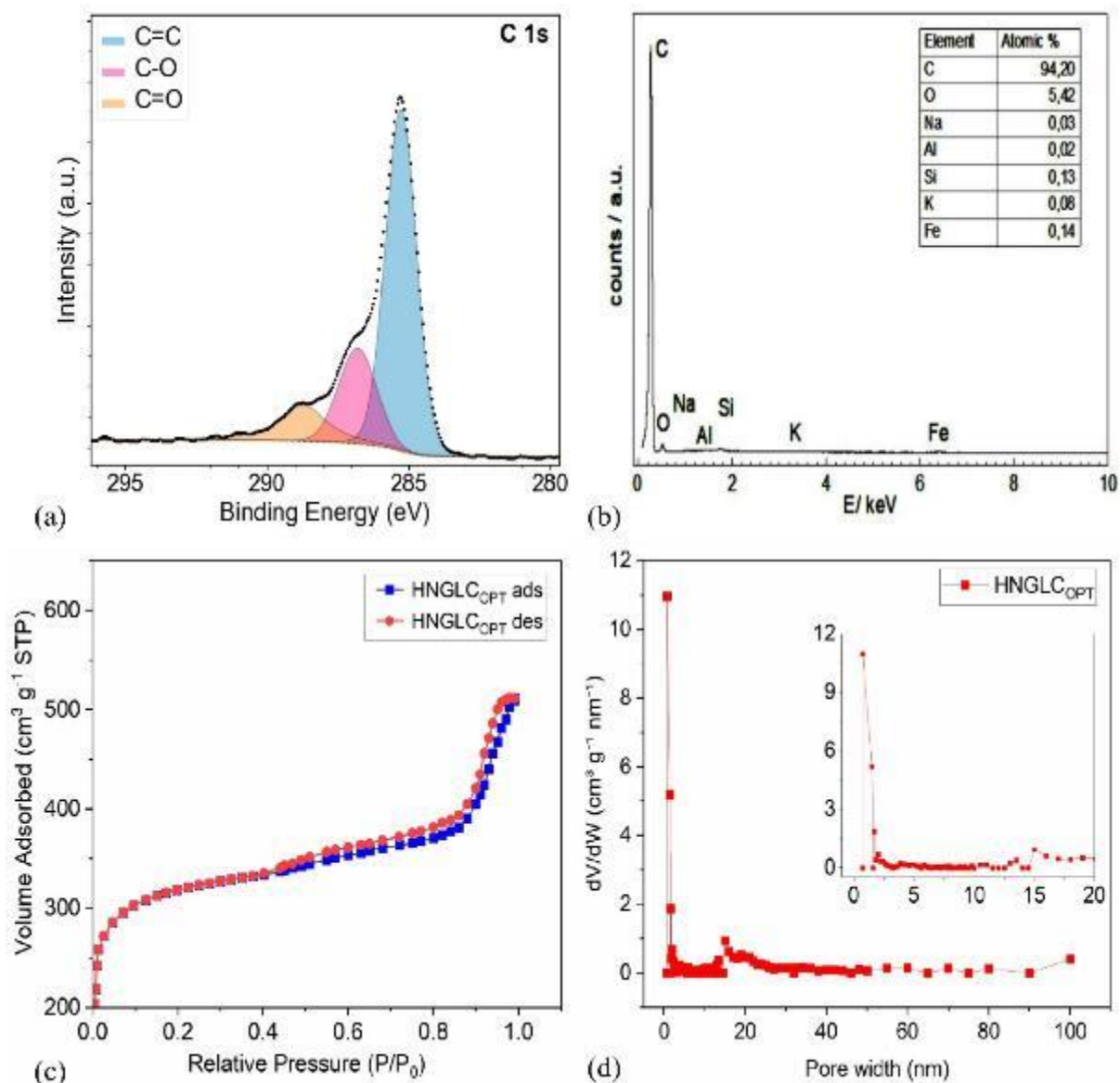


Figure 14. Chemical, compositional, and textural characterization of the optimized GLC sample, showing (a) the XPS C1s spectrum, (b) EDX spectrum, (c) nitrogen adsorption–desorption isotherm, and (d) pore size distribution with an enlarged inset [104].

Overall, the combined structural analyses confirm that the optimized synthesis conditions yielded a hierarchically porous, graphene-like carbon with partially ordered graphitic domains.

4.1.4 Electrochemical Performance of GLC-OPT

Electrochemical evaluation of GLC-OPT was performed to assess the accessibility and charge-storage behavior of the optimized porous graphitic framework. The electrochemical response of the material in a symmetric supercapacitor configuration is presented in Figure 15.

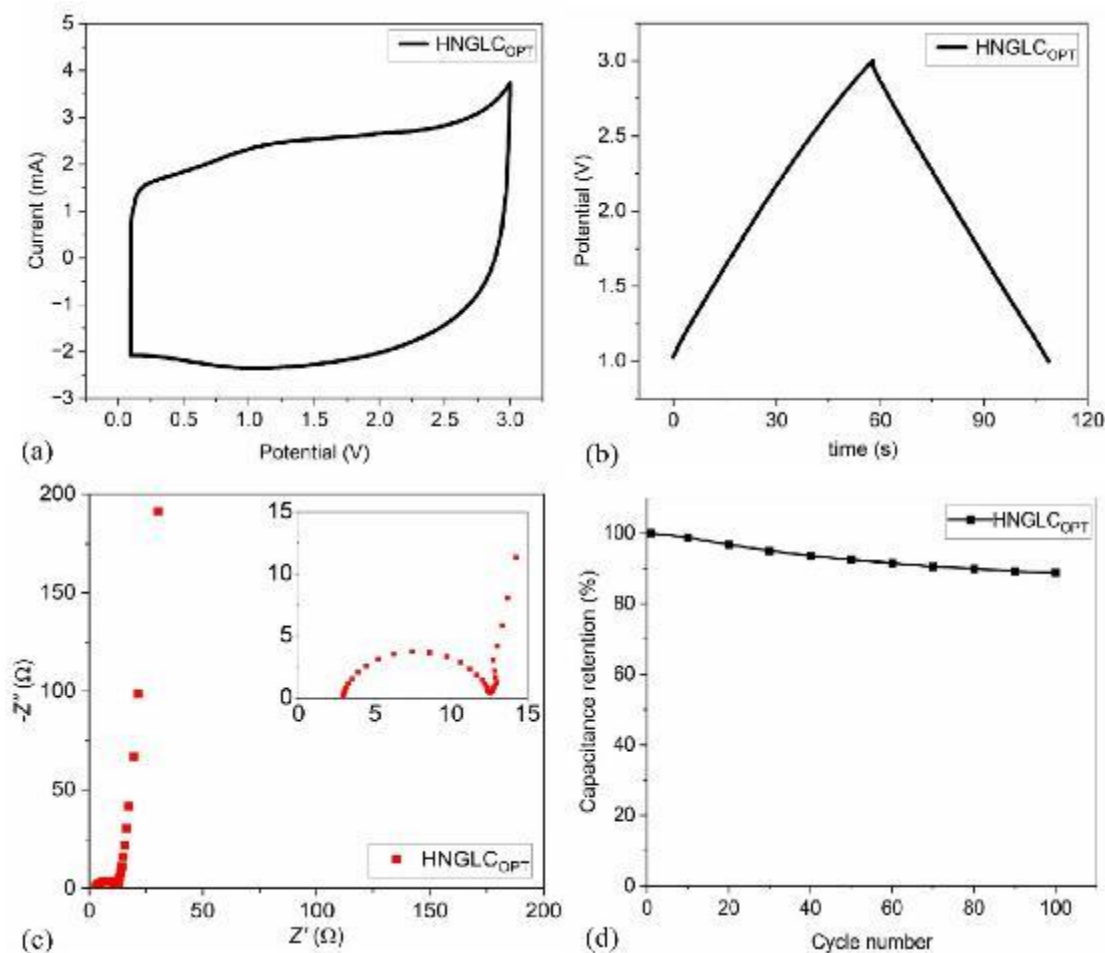


Figure 15. Electrochemical evaluation of GLC-OPT, including (a) cyclic voltammetry curves, (b) galvanostatic charge–discharge profiles, (c) Nyquist impedance spectrum, and (d) cycling stability [104].

The cyclic voltammograms shown in Figure 13a exhibited near-rectangular profiles within the investigated voltage window, indicating predominantly capacitive charge-storage behavior with efficient ion transport throughout the porous electrode network [5, 7]. The absence of pronounced

redox peaks suggests that the electrochemical response was dominated primarily by electric double-layer capacitance[5].

Galvanostatic charge–discharge curves presented in Figure 15b displayed relatively symmetrical triangular profiles with limited voltage drop, indicating stable and reversible charge-storage behavior[5].

The Nyquist impedance spectrum shown in Figure 15c exhibited a relatively small semicircle at high frequencies, followed by a near-vertical response characteristic of porous capacitive materials [7]. The relatively low equivalent series resistance indicates efficient ion and electron transport within the electrode structure.

Cycling stability results presented in Figure 15d further demonstrated relatively stable electrochemical behavior during repeated charge–discharge cycling, indicating that the porous graphitic framework retained structural integrity under electrochemical operating conditions [126].

The key electrochemical performance parameters extracted from the electrochemical measurements are summarized in Table 17.

Table 17: Electrochemical performance parameters of GLC-OPT in symmetric supercapacitor configuration.

Parameter	Value
CV specific capacitance	53.1 F g ⁻¹
GCD specific capacitance	41.95 F g ⁻¹
Equivalent series resistance (ESR)	2.8 Ω
Energy density	5.78 Wh kg ⁻¹
Power density	637 W kg ⁻¹
Cycling retention after 100 cycles	88.8%
Operating voltage window and current	0 – 3 / 5mA

Overall, the electrochemical results confirm that the optimized synthesis strategy successfully produced a graphene-like carbon architecture capable of supporting efficient ion transport, stable capacitive behavior, and favorable charge-transfer characteristics.

4.2 Alternative Activation and Catalytic Reconstruction Pathways

Beyond the primary KOH-based activation route described in Section 4.1, alternative activation and catalytic reconstruction pathways were explored to assess the effects of phosphoric acid activation and ZnCl_2 -assisted reconstruction on the structural and electrochemical development of biomass-derived graphene-like carbon materials. In contrast to the direct KOH activation method, these alternative systems utilized hydrothermal carbonization followed by H_3PO_4 activation and subsequent high-temperature ferrocene-catalyzed reconstruction [14, 127, 128]. The results presented in this section are predominantly based on another recently published work by the author [129], which is also part of the present dissertation.

The goal of this investigation is to determine whether phosphorus-mediated stabilization and ZnCl_2 -assisted textural regulation could facilitate graphitic reconstruction while maintaining accessible porous architecture. Specifically, the relationships among Fe-mediated graphitization, pore redistribution, structural disorder, and charge-transport behavior are examined [16, 130, 131].

4.2.1 Influence of H_3PO_4 Activation and ZnCl_2 -Assisted Reconstruction

The progression from hydrothermal carbon (HTC) to phosphoric acid-activated carbon (HTC-PA), Fe-reconstructed activated carbon without ZnCl_2 assistance (HTC-PA-Fe), and ZnCl_2 -assisted phosphorus-mediated reconstructed carbon (HTC-PA-ZnFe) was examined to elucidate the influence of activation chemistry and catalytic restructuring on carbon architecture.

Figure 16 presents representative SEM images and corresponding EDX spectra. The HTC precursor exhibited a compact, irregular morphology typical of partially carbonized lignocellulosic biomass [12, 43]. After H_3PO_4 activation, significant restructuring of the carbon matrix was observed, resulting in interconnected porous channels and sponge-like surface textures attributed to acid-mediated dehydration and chemical etching [14, 132].

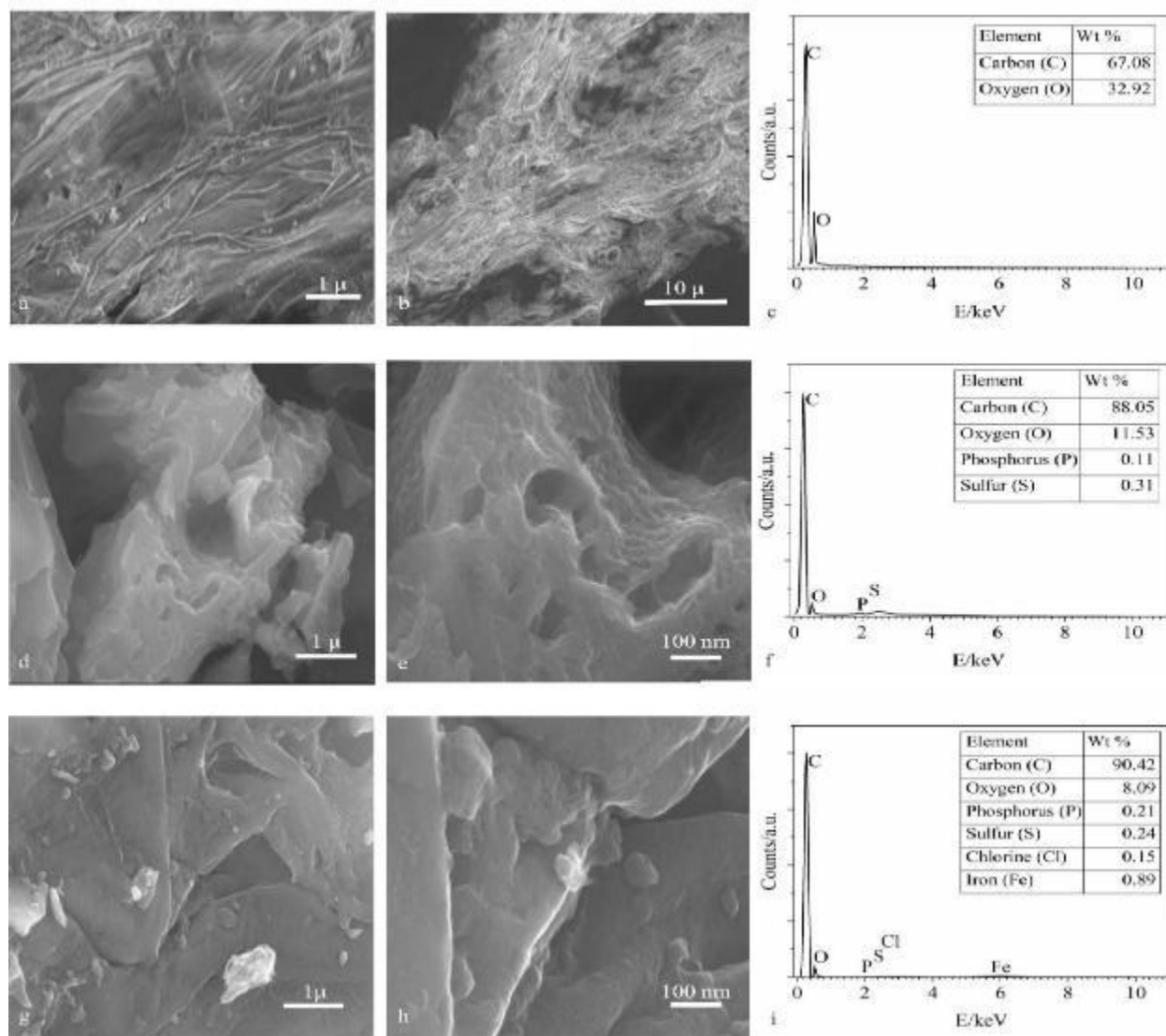


Figure 16. SEM images and corresponding EDX spectra of (a–c) HTC, (d–f) HTC-PA, (g–i) HTC-PA-Fe, and (j–l) HTC-PA-Fe illustrating morphological and compositional evolution during activation and catalytic reconstruction [129].

Catalytic reconstruction induced additional morphological changes in the activated carbon framework. The HTC-PA-Fe sample exhibited partial surface smoothing and localized restructuring following thermal treatment, indicative of catalytic rearrangement within the carbon matrix [16, 133]. Conversely, the ZnCl_2 -assisted HTC-PA-ZnFe sample retained the porous scaffold and exhibited more interconnected, refined surface features, suggesting that ZnCl_2 -assisted reconstruction enabled controlled pore evolution while preventing significant framework collapse [128, 130].

Elemental analysis revealed progressive compositional changes throughout activation and reconstruction. Carbon content increased after thermal reconstruction, while oxygen content decreased as a result of high-temperature deoxygenation [134, 135]. Residual phosphorus species remained detectable after reconstruction, indicating the persistence of phosphorus-containing functionalities within the carbon framework [128, 136]. The detection of trace iron in HTC-PA-ZnFe further confirmed the involvement of catalytic species during graphitic reconstruction [16, 17].

Transmission electron microscopy (TEM) analysis offered additional insight into nanoscale structural evolution (Figure 17). HTC-PA was composed mainly of disordered carbon domains with minimal local ordering [43]. In contrast, HTC-PA-ZnFe displayed interconnected carbon clusters containing filamentous graphitic features embedded within the porous matrix [16, 137].

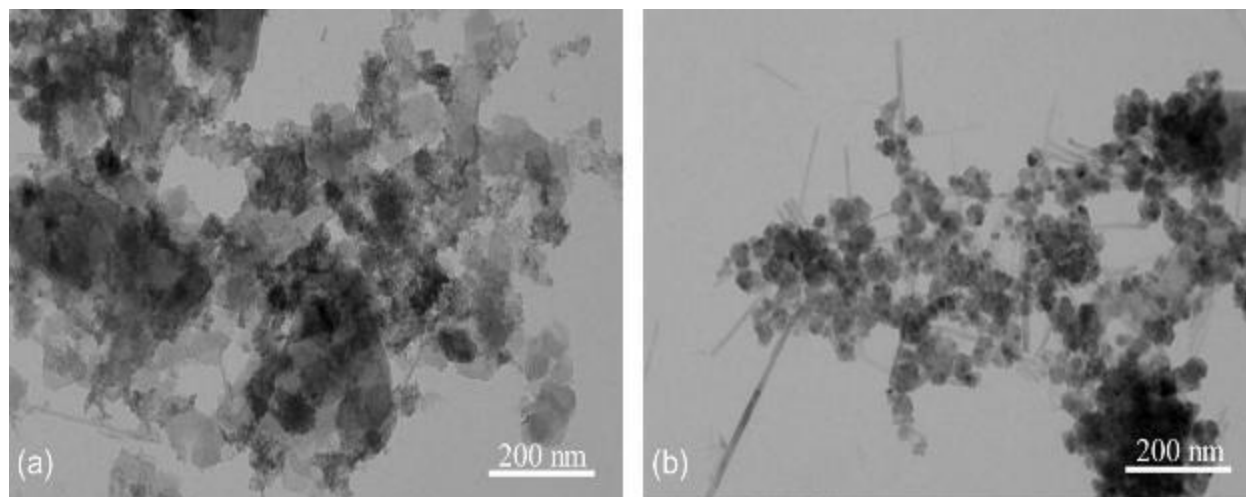


Figure 17. TEM images of (a) HTC-PA and (b) HTC-PA-ZnFe illustrating nanoscale structural evolution during catalytic reconstruction.

The presence of these localized graphitic domains indicates that catalytic reconstruction facilitated partial ordering while maintaining the surrounding disordered porous architecture [16].

The structural evolution of the reconstructed materials was further examined using XRD and Raman spectroscopy (Figure 18), with the derived structural parameters summarized in Table 18.

HTC-PA exhibited broad diffraction features indicative of highly disordered porous carbon [138]. After catalytic reconstruction, both HTC-PA-Fe and HTC-PA-ZnFe demonstrated improved graphitic ordering, as evidenced by more distinct graphitic reflections and lower Raman I_D/I_G ratios [7, 16]. The lateral crystallite size (L_a) increased progressively from HTC-PA to HTC-PA-ZnFe, indicating enhanced in-plane ordering during Fe-mediated reconstruction [16, 139].

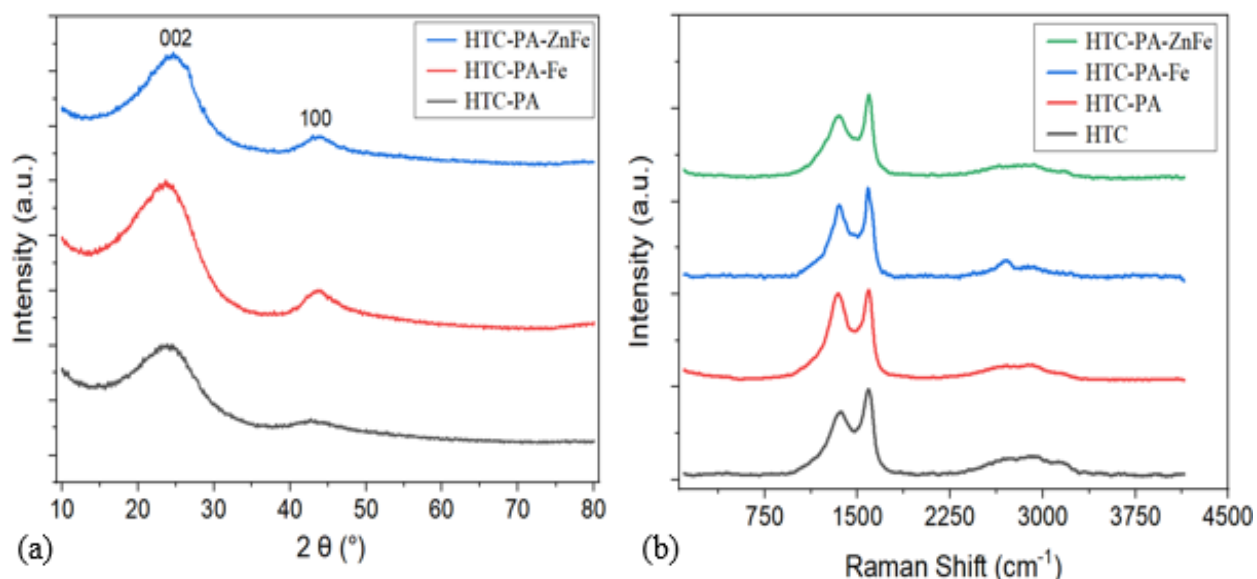


Figure 18. (a) XRD patterns and (b) Raman spectra of HTC, HTC-PA, HTC-PA-Fe, and HTC-PA-ZnFe showing structural evolution during catalytic reconstruction [129]. Raman deconvolution spectra are provided in Figure A1 (Appendix B).

Although lateral ordering improved, the interlayer spacing (d_{002}) remained relatively large (approximately 0.36 nm) compared with crystalline graphite [13, 138, 140]. This observation indicates that reconstruction primarily resulted in partial graphitic organization rather than complete graphitic stacking. The persistence of phosphorus-containing interfacial species likely limited excessive densification during thermal treatment, thereby preserving turbostratic character and preventing severe structural collapse [128, 141].

Raman spectral deconvolution further confirmed progressive ordering, accompanied by the persistence of defect-rich domains. While disorder-related Raman contributions decreased following reconstruction, significant structural disorder remained, attributable to retained porosity and incomplete graphitic stacking [142, 143].

Table 18. Raman- and XRD-derived structural parameters of reconstructed carbon materials.

Sample	I_D/I_G	L_a (nm)	L_c (nm)	d_{002}
HTC	0.75	—	—	—
HTC-PA	0.95	20.20	1.03	0.372
HTC-PA-Fe	0.81	23.73	1.18	0.360
HTC-PA-ZnFe	0.74	26.01	1.17	0.362

Nitrogen adsorption–desorption analysis revealed substantial textural redistribution following catalytic reconstruction (Figure 19 and Table 19).

Although catalytic treatment reduced the total BET surface area compared to HTC-PA, the HTC-PA-ZnFe sample demonstrated an increased microporous contribution, indicating selective pore refinement rather than complete pore collapse [125, 130]. In contrast, HTC-PA-Fe experienced a greater loss of surface area without notable micropore enhancement, suggesting that Fe-mediated reconstruction alone was insufficient to preserve highly accessible pore architecture [131]. Because N₂ adsorption mainly reflects the accessible micro- and mesopore network, to assess the narrower micropores, CO₂ adsorption at 273 K was performed. HTC-PA-ZnFe showed higher CO₂ uptake at low pressure than HTC-PA (Figure 20d), indicating greater ultramicropore accessibility. This is consistent with the NLDFT pore size distributions (Figure A2), which show a larger contribution from pores in the 3.6–5.6 Å range for HTC-PA-ZnFe. The CO₂-derived surface area also increased from 107 m² g^{−1} for HTC-PA to 117 m² g^{−1} for HTC-PA-ZnFe, further indicating improved accessibility of ultramicropores following catalytic reconstruction.

The ZnCl₂-assisted pathway appears to have facilitated selective removal of unstable mesoporous regions while stabilizing narrow microporous domains [128, 130]. This controlled redistribution of porosity enhanced micropore accessibility, despite a partial reduction in overall surface area.

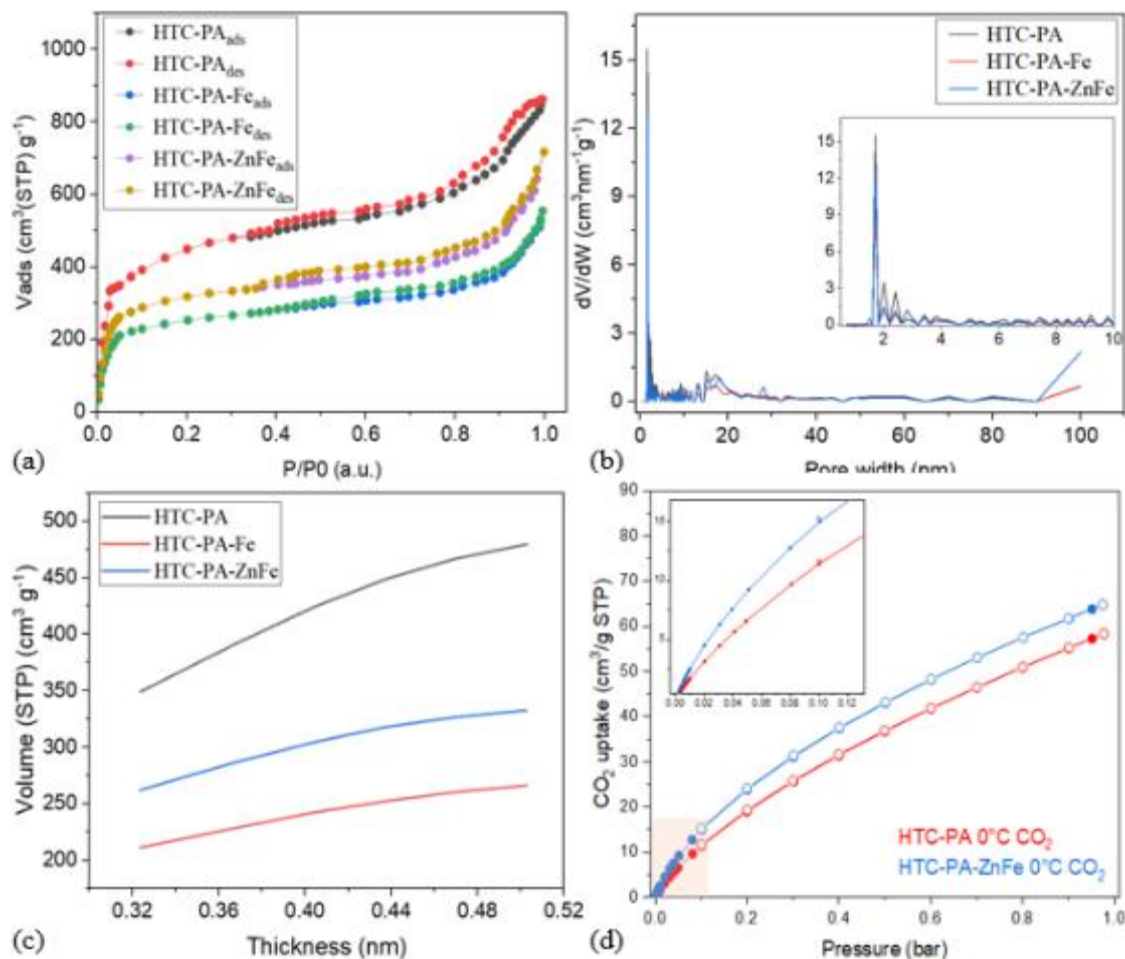


Figure 19. Nitrogen adsorption–desorption isotherms (a), pore size distributions (b), t-plot analysis (c), and CO₂ adsorption isotherms (d) of HTC-PA, HTC-PA-Fe, and HTC-PA-ZnFe, showing changes in pore characteristics following catalytic reconstruction.

Table 19: Textural parameters of reconstructed carbon materials derived from nitrogen adsorption–desorption analysis.

Parameter	HTC-PA	HTC-PA-Fe	HTC-PA-ZnFe
Total BET surface area ($\text{m}^2 \text{g}^{-1}$)	1487.41	814.36	1022.32
External surface area ($\text{m}^2 \text{g}^{-1}$)	1154.25	482.95	624.98
Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	0.18	0.18	0.21

Figure 20a presents the FTIR spectra of HTC, HTC-PA, HTC-PA-Fe, and HTC-PA-ZnFe. Based on observation, HTC exhibited the strongest oxygen-related bands, indicating the presence of abundant oxygen-containing functional groups. Following H_3PO_4 activation and carbonization,

these bands remarkably decreased in HTC-PA, reflecting progressive deoxygenation and carbonization. Following catalytic treatment with ferrocene (HTC-PA-Fe) and the combined ferrocene/ ZnCl_2 treatment (HTC-PA-ZnFe), further reduction in oxygen-related bands was observed, suggesting additional removal of oxygen-containing functionalities and continued structural evolution of the carbon framework [42, 49].

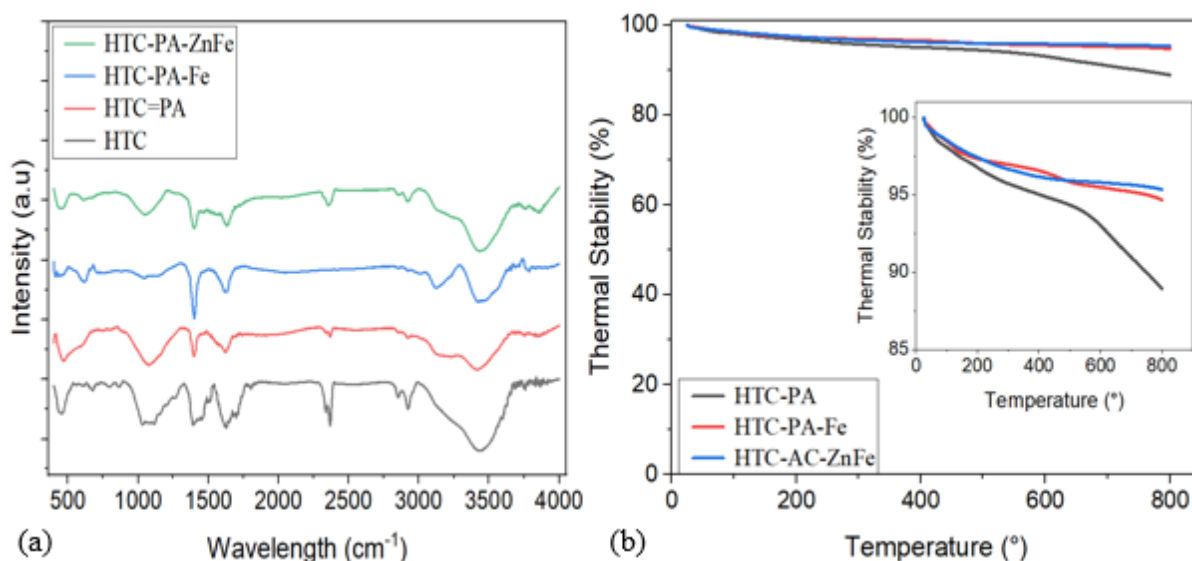


Figure 20. (a) FTIR spectra of hydrochar (HTC), phosphoric acid-activated carbon (HTC-PA), Fe-catalyzed carbon (HTC-PA-Fe), and Fe/ ZnCl_2 -treated carbon (HTC-PA-ZnFe). (b) TGA curves of HTC-PA, HTC-PA-Fe, and HTC-PA-ZnFe under N_2 atmosphere.

FTIR (Figure 20a) and TGA (Figure 20b) were used respectively to track changes in functional groups and thermal stability. FTIR revealed a steady decrease in oxygen-containing groups from HTC to HTC-PA, HTC-PA-Fe, and HTC-PA-ZnFe, consistent with progressive deoxygenation as treatment continued. All samples exhibited high thermal stability under N_2 up to the full temperature range probed (0–800 $^{\circ}\text{C}$). Of the three, HTC-PA-ZnFe retained the highest residual mass, followed closely by HTC-PA-Fe, whereas HTC-PA showed the lowest mass retention. The improved thermal stability of the catalytically treated samples is an indication that the Fe-assisted treatments resulted in the development of more thermally stable carbon structures, consistent with

the structural reorganization commonly observed during catalytic graphitization of carbon materials [16, 49].

The high-resolution XPS spectra (Figure 21) provided further insight into the structural evolution of the reconstructed materials. The C 1s and O 1s spectra revealed the coexistence of graphitic carbon environments, oxygen-containing functionalities, and phosphorus-related species within the carbon framework. Compared with HTC-PA, the catalytically treated samples exhibited a greater contribution from graphitic carbon, reflecting increased structural ordering. For HTC-PA-ZnFe, the appearance of Fe₃C-related contributions provides evidence for iron-mediated graphitization, where iron species facilitate carbon dissolution and reprecipitation during thermal treatment [16, 49]. The O 1s spectra also showed contributions associated with phosphorus-derived oxygen environments, indicating that these species remained within the material after the high-temperature treatment. The Fe-containing sample without ZnCl₂ retained a mixture of carbon and oxygen-containing environments, whereas the ZnFe treatment showed the additional Fe₃C contribution. The retention of phosphorus-containing species in combination with the development of graphitic domains suggests that catalytic reconstruction did not simply remove surface functionalities but produced a carbon structure containing both ordered carbon regions and stable phosphorus-derived interfacial species.

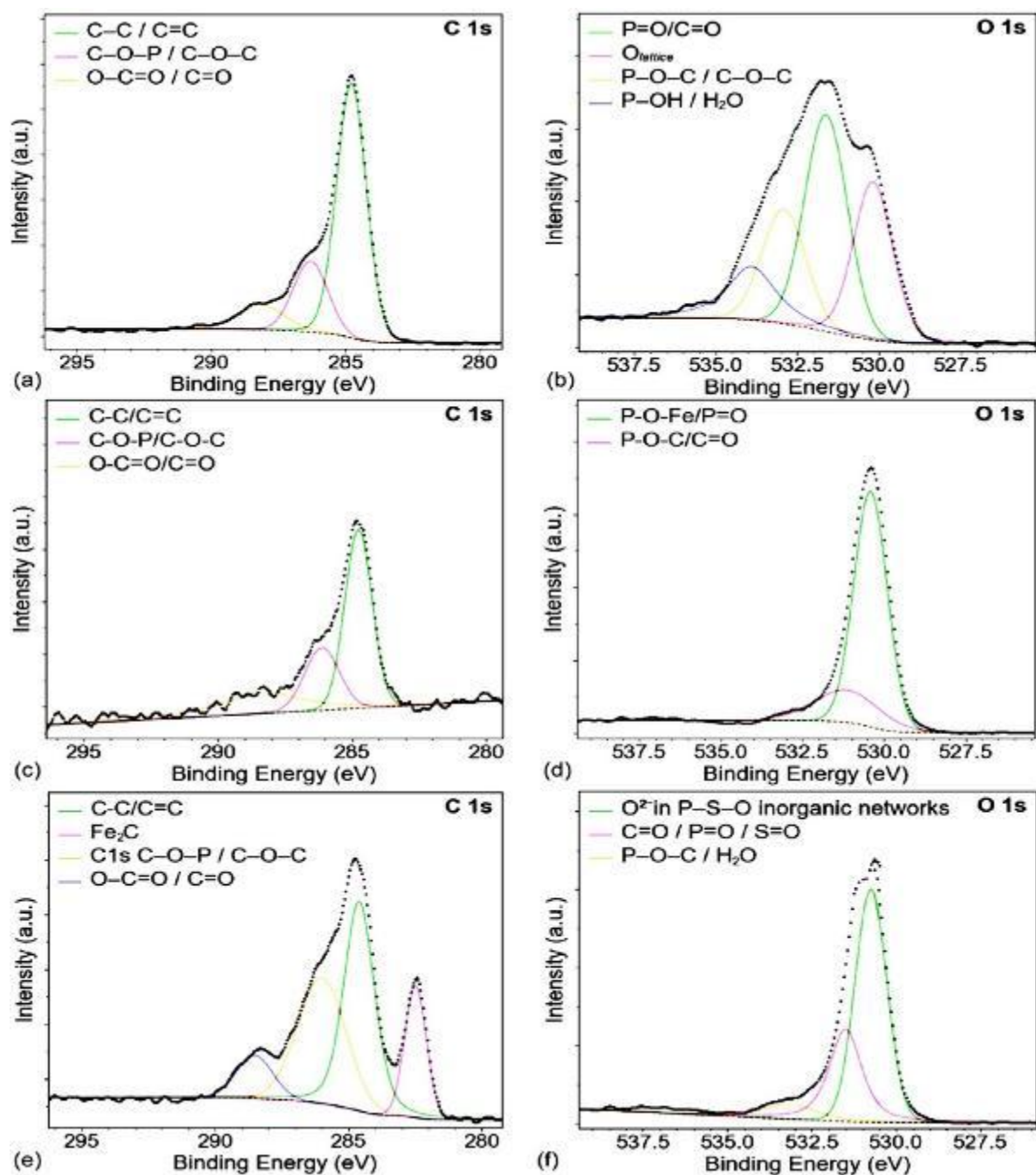


Figure 21. High-resolution XPS spectra of the C 1s and O 1s regions for HTC-AC (a, b), HTC-AC-Fe (c, d), and P-TCH (e, f). HTC-AC-Fe is included as a control to isolate the effect of Fe treatment without ZnCl₂ [129]. P 2p spectra are provided in Appendix B Figure A3.

In summary, the combined H₃PO₄ activation and ZnCl₂-assisted catalytic reconstruction pathway yielded a structurally coherent yet highly accessible turbostratic carbon framework. Unlike

conventional catalytic graphitization methods, which often lead to significant pore collapse [144-147], the phosphorus-mediated, ZnCl_2 -assisted strategy promoted localized graphitic ordering while preserving accessible microporosity and structural stability.

4.2.2 Electrochemical Evaluation of Reconstructed Carbon Materials

Electrochemical characterization was conducted to assess the effects of phosphoric acid activation and catalytic reconstruction on charge storage behavior, ion transport, and internal resistance. Comparative electrochemical responses of HTC-PA, HTC-PA-Fe, and HTC-PA-ZnFe are shown in Figure 22, with the corresponding electrochemical and structural parameters summarized in Table 20.

The cyclic voltammograms in Figure 22a indicate that HTC-PA and HTC-PA-ZnFe maintained relatively stable capacitive behavior, whereas HTC-PA-Fe exhibited a weaker electrochemical response despite lower resistance. These results suggest that catalytic reconstruction enhanced conductivity but did not necessarily preserve the accessible porous structure required for efficient charge storage [4, 6, 20].

The galvanostatic charge–discharge profiles in Figure 22b further support this interpretation. HTC-PA-ZnFe exhibited a discharge response comparable to HTC-PA, despite having a lower total BET surface area, indicating more effective utilization of the remaining accessible porosity [6, 29].

The electrochemical response was strongly influenced by the balance among conductivity, accessible porosity, and structural ordering. HTC-PA achieved a specific capacitance of 149.08 F g^{-1} but exhibited a relatively high equivalent series resistance (ESR) of $5.73 \text{ } \Omega$, indicating limited electronic conductivity within the highly porous yet poorly ordered carbon framework [4].

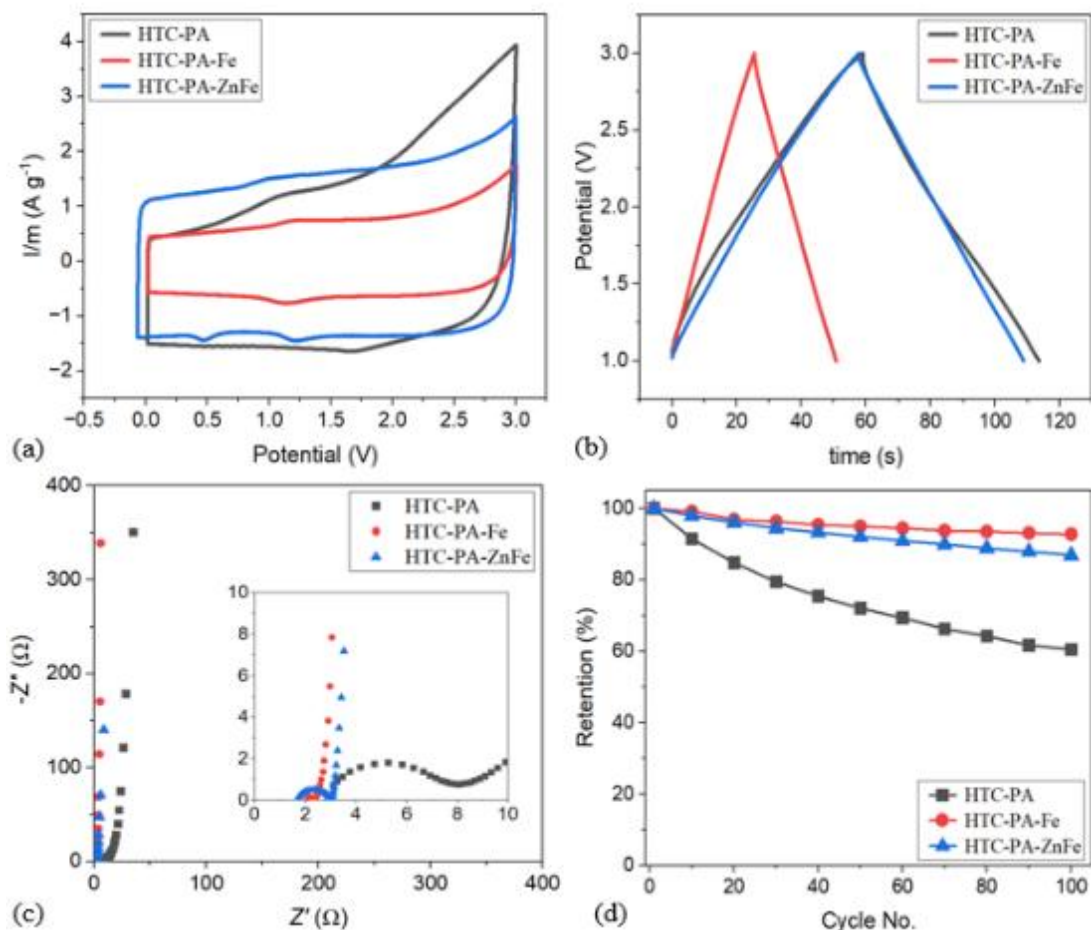


Figure 22. Electrochemical diagnostics of HTC-PA, HTC-PA-Fe, and HTC-PA-ZnFe: (a) CV response, (b) GCD profiles, (c) Nyquist impedance spectra with inset highlighting the low-resistance region, and (d) cycling retention.

HTC-PA-Fe exhibited the lowest ESR (2.17 Ω), confirming improved conductivity following Fe-mediated reconstruction. However, its capacitance decreased to 64.01 F g⁻¹. This reduction demonstrates that enhanced conductivity alone was insufficient to offset the loss of accessible surface area and reduced pore utilization [6, 20].

In contrast, HTC-PA-ZnFe maintained a high specific capacitance of 148.92 F g⁻¹ while reducing ESR to 2.69 Ω. These results indicate that ZnCl₂-assisted reconstruction enhanced charge transport without significantly compromising ion-accessible porosity. Although HTC-PA-ZnFe had a lower

total BET surface area than HTC-PA, its increased microporous contribution and BET-normalized surface efficiency suggest more effective utilization of the available surface for electrochemical charge storage [6, 29].

Table 20: Diagnostic electrochemical and structural parameters of HTC-PA, HTC-PA-Fe, and HTC-PA-ZnFe.

Parameter	HTC-AC	HTC-PA-Fe	HTC-PA-ZnFe	Observed Trend	Likely Contributing Factors
ESR (Ω) from GCD	5.73	2.17	2.69	HC-AC > Fe-AC $\approx$ P-TCH	Fe-mediated conductivity
Area	10.02	7.85	14.57	P-TCH > HC-AC > Fe-AC	Pore accessibility + ordering
Efficiency ($\mu F\ cm^{-2}$)					
Retention (%)	60.49	92.77	86.90	Fe-AC $\geq$ P-TCH > HC-AC	Structural stability
Micropore Area ($m^2\ g^{-1}$)	333.15	331.41	397.34	P-TCH > HC-AC $\approx$ Fe-AC	Textural redistribution

The Nyquist plots in Figure 22c corroborate this interpretation. Compared with HTC-PA, both HTC-PA-Fe and HTC-PA-ZnFe exhibited reduced internal resistance, confirming the beneficial effect of Fe-mediated reconstruction on electronic transport [53]. However, the lower capacitance of HTC-PA-Fe demonstrates that improved charge transfer alone does not ensure higher energy-storage performance. Efficient electrochemical behavior requires both the preservation of accessible microporosity and the formation of conductive pathways [4, 6].

Cycling stability (Figure 22d) followed the trend HTC-PA-Fe > HTC-PA-ZnFe > HTC-PA. The high retention observed for HTC-PA-Fe suggests that catalytic treatment enhanced structural stability, while the strong capacitance retention of HTC-PA-ZnFe indicates that $ZnCl_2$ -assisted reconstruction preserved both mechanical stability and electrochemically active porosity. HC-AC

exhibited lower retention, consistent with a more disordered and less electronically coherent porous framework [6, 148].

Overall, HTC-PA-ZnFe exhibited the most balanced electrochemical response among the reconstructed materials, combining high capacitance, reduced internal resistance, improved area-normalized surface efficiency, and strong cycling retention. These findings indicate that the superior performance of HTC-PA-ZnFe resulted from the combined effects of catalytic reconstruction, phosphorus-mediated structural stabilization, and ZnCl_2 -assisted textural refinement, rather than from graphitization alone [6, 29, 148].

The comparative electrochemical results further demonstrate the suitability of the reconstructed architecture for subsequent modification studies. Although HTC-PA-Fe exhibited improved conductivity, its reduced capacitance indicated insufficient utilization of accessible surface area. In contrast, HTC-PA-ZnFe maintained high charge-storage capability while enhancing transport characteristics, establishing it as the most suitable reconstructed carbon platform for further functionalization and heteroatom-doping investigations [4, 6].

4.3 Graphene Oxide (GO) and Reduced Graphene Oxide (rGO)

This section discusses the synthesis optimization, structural evolution, and oxidation behavior of graphene oxide synthesized from biographite using the modified Tour method [62, 149]. Emphasis is placed on identifying oxidation conditions that produce a balanced graphene oxide precursor suitable for subsequent reduction and electrochemical applications. The influence of oxidation severity on oxygen functionalization, structural disorder, and graphitic preservation was systematically evaluated using Raman spectroscopy and X-ray Photoelectron Spectroscopy (XPS).

4.3.1 Optimization of GO Synthesis Using the Modified Tour Method

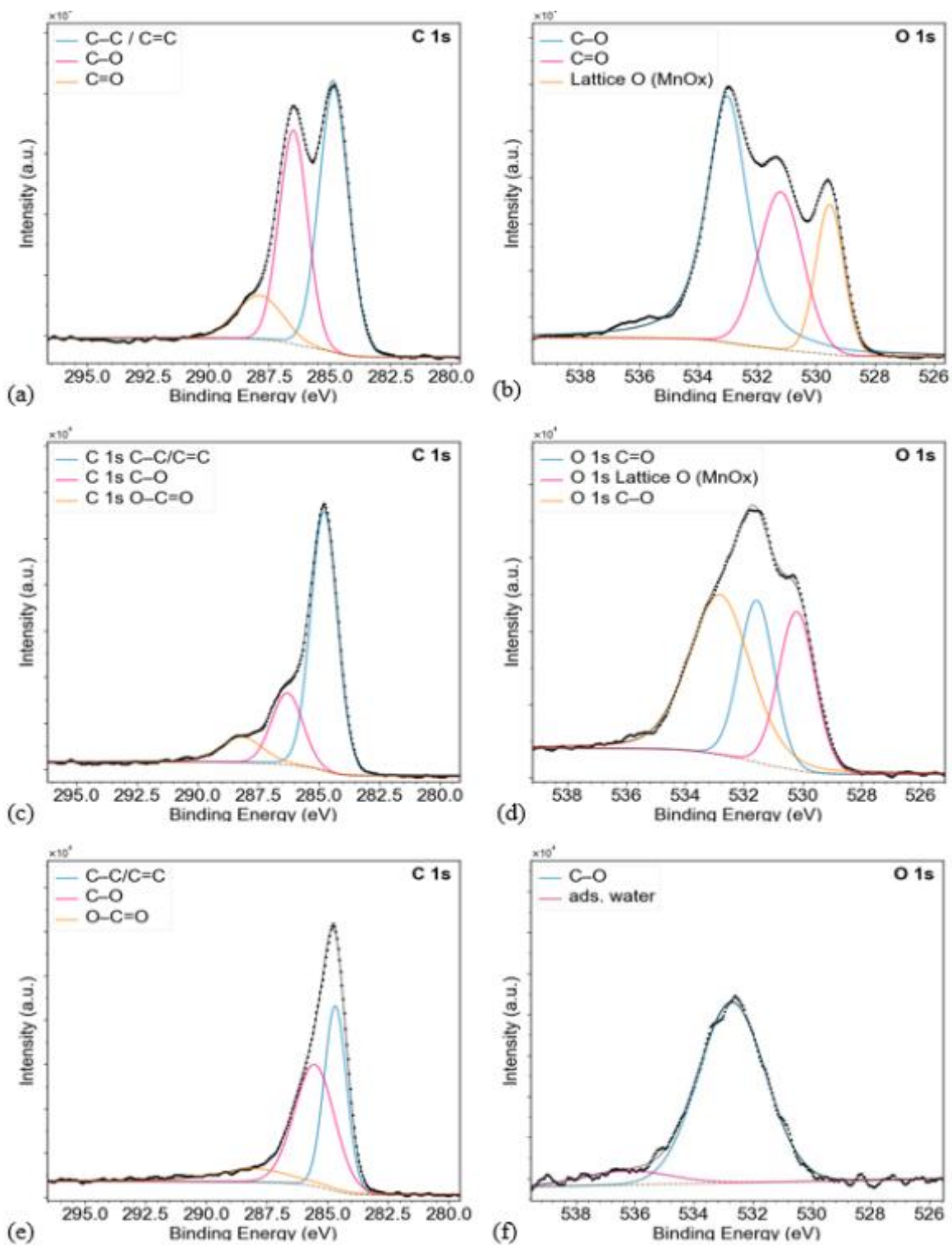
4.3.1.1 Response Variability Across the L9 Experimental Matrix

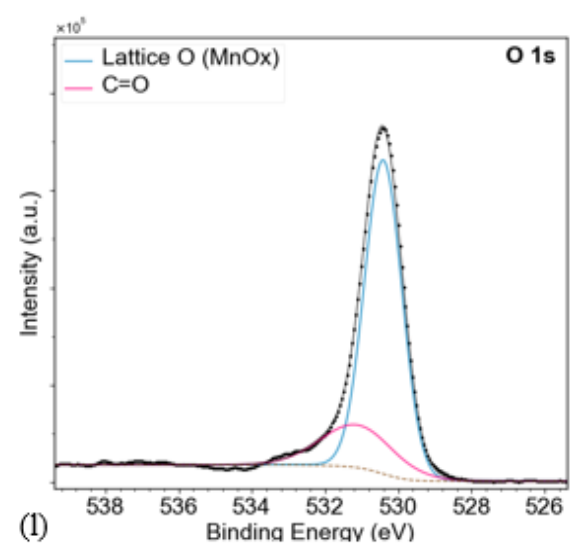
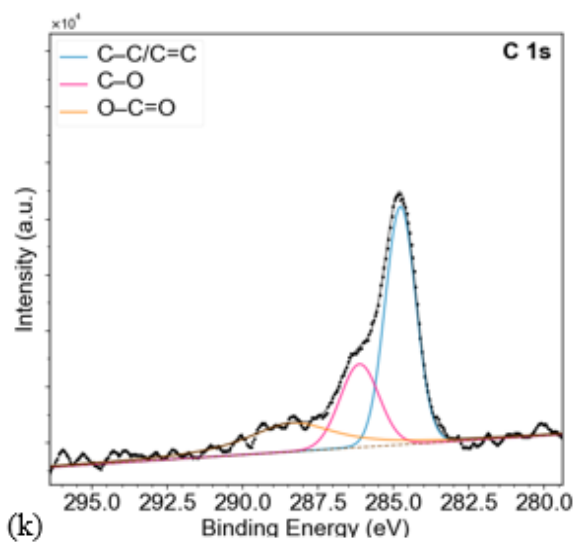
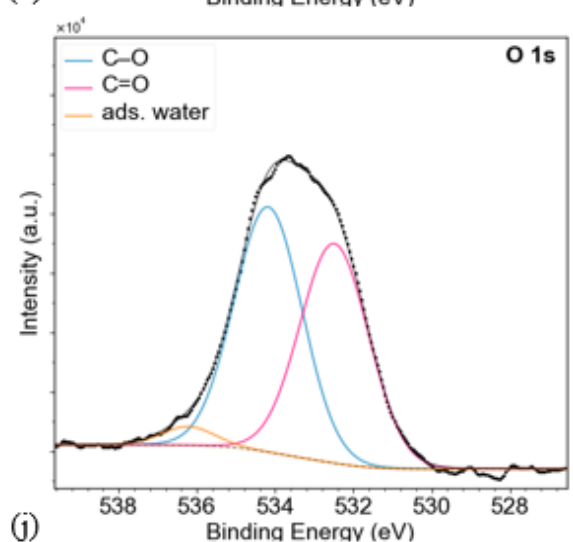
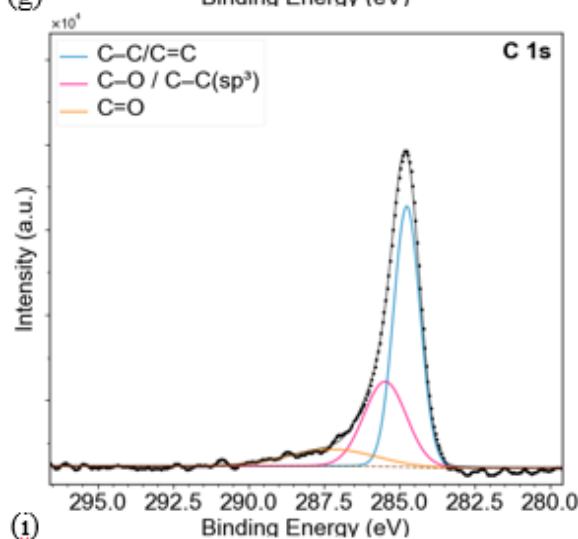
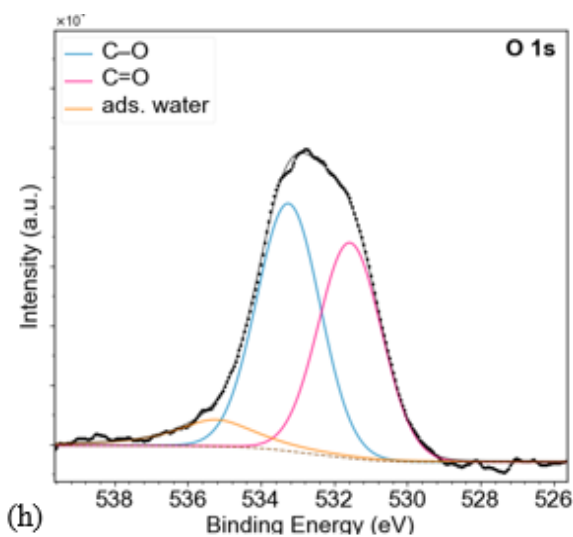
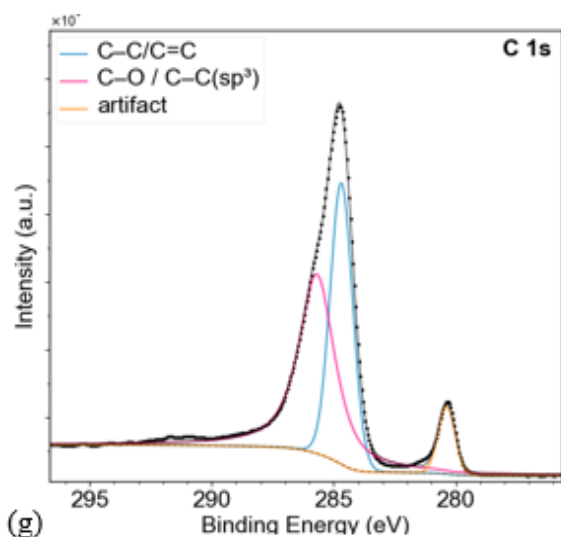
The influence of oxidation parameters on graphene oxide formation was evaluated using the L9 Taguchi orthogonal array and the GO synthesis procedure described in sections 3.2 and 3.4, respectively. Significant variation in oxidation degree and structural disorder was observed across the experimental matrix, confirming the strong dependence of GO formation on oxidant loading, acid composition, oxidation temperature, and reaction duration. The measured responses for all experimental runs are summarized in Table 21, while the XPS analyses are presented in Figure 23, with others in the supplementary information.

Table 21. L9 orthogonal array design and measured responses for graphene oxide synthesized via the modified Tour method.

Run	KMnO ₄ dosage (g)	Acid ratio	Temperature (°C)	Time (h)	O/C ratio	I _D /I _G
1	5	3	40	6	0.55	0.94
2	5	6	50	9	0.38	1.04
3	5	9	60	12	0.16	1.06
4	6	3	50	12	0.43	0.89
5	6	6	60	6	0.48	1.05
6	6	9	40	9	0.85	0.99
7	7	3	60	9	1.12	1.12
8	7	6	40	12	1.04	1.01
9	7	9	50	6	1.30	0.90

The XPS-derived O/C ratio varied substantially from 0.16 to 1.30, indicating the formation of graphene oxide structures spanning low, intermediate, and highly oxidized regimes. The broad oxidation distribution suggests heterogeneous oxygen incorporation within the biographite precursor, likely associated with differences in graphitic ordering and local accessibility of oxidation sites [150, 151].





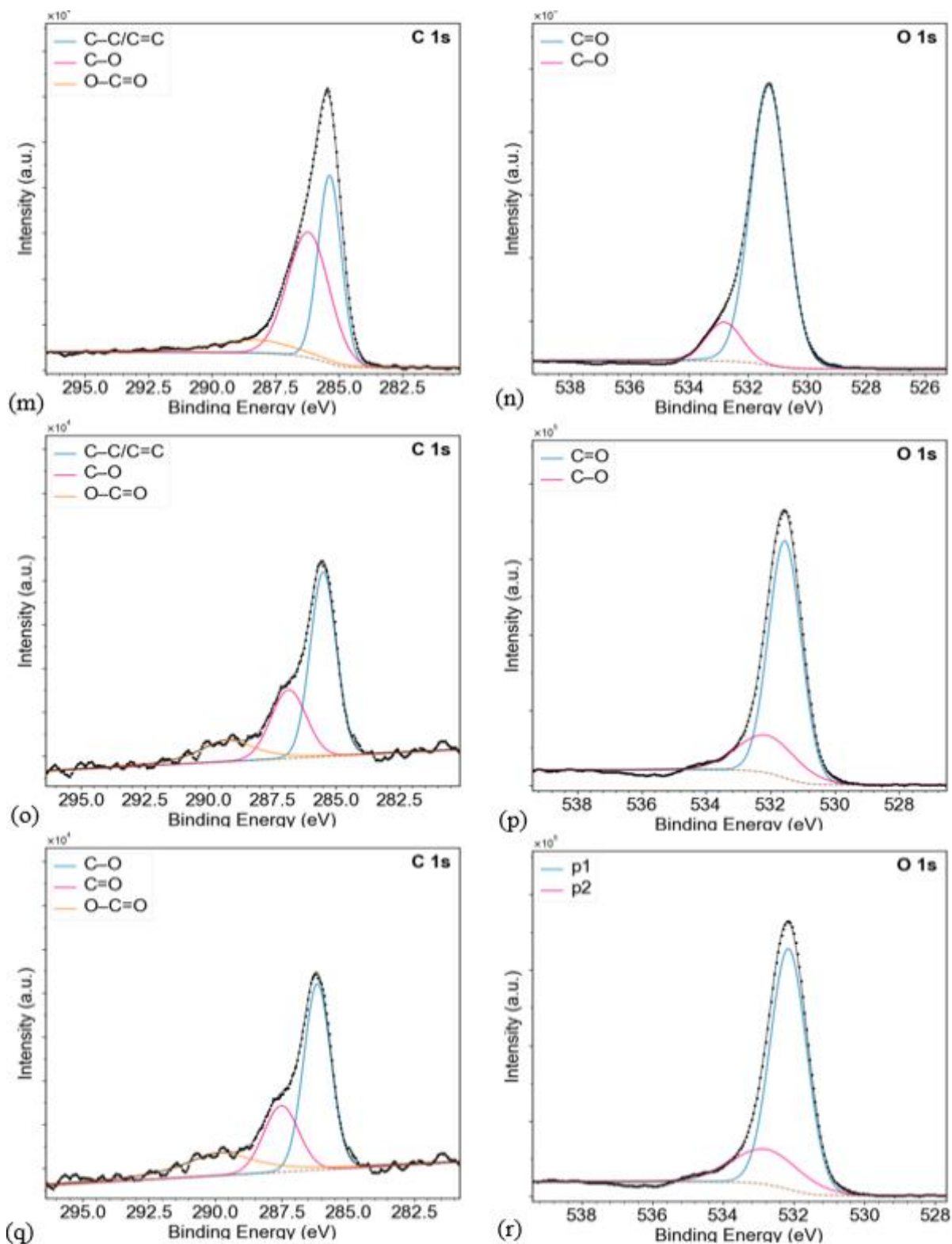


Figure 23. High-resolution XPS analysis of nine GO samples, presenting the C 1s and O 1s deconvoluted spectra for each material synthesized under different Taguchi conditions. Panels a–b represent sample 1, c–d sample 2, and this pattern continues through q–r for sample 9.

Runs 1–5 generally exhibited moderate oxygen incorporation ($O/C = 0.38\text{--}0.55$), corresponding to partially oxidized graphene oxide structures with relatively preserved graphitic domains. In contrast, Runs 7–9 exhibited significantly higher oxygen content ($O/C > 1.0$), indicating highly oxygen-enriched surfaces and substantial disruption of the sp^2 carbon framework [151, 152]. The Raman I_D/I_G ratio also varied considerably across the experimental matrix, ranging from 0.89 to 1.12. Lower I_D/I_G values indicate greater graphitic preservation, whereas higher values reflect increased structural disorder generated during oxidation [152, 153]. The simultaneous increase in O/C and I_D/I_G ratio that was observed under more aggressive oxidation conditions confirms that severe oxidation promoted both oxygen functionalization and carbon lattice disruption [154, 155].

This behavior can be understood in terms of progressive oxidation of the graphitic lattice, where permanganate-driven oxidation introduces oxygen-containing functional groups such as hydroxyl, epoxy, carbonyl, and carboxyl species onto both basal planes and edge sites [150, 151]. Initial oxidation preferentially occurs at defect sites and grain boundaries, while continued oxidation extends into the basal plane, progressively converting sp^2 -hybridized carbon into sp^3 -like configurations [150–152]. This transition disrupts π -electron delocalization, leading to increased defect density as reflected by the rise in I_D/I_G ratio [151, 152]. At higher oxidation severity, further structural breakdown and partial fragmentation of graphitic domains occur [151, 152], which contributes to elevated O/C ratios but simultaneously reduces the continuity of conjugated carbon networks essential for electronic transport in the reduced material [77, 151, 156].

Importantly, the results reveal that higher oxidation severity did not necessarily produce structurally optimal graphene oxide. While elevated oxidant concentration and acid strength enhanced oxygen incorporation [157, 158], excessively oxidized samples exhibited substantial

disorder that may negatively influence conductivity restoration during subsequent reduction [77, 159]. The Raman spectra of all the samples are shown in Figure 24.

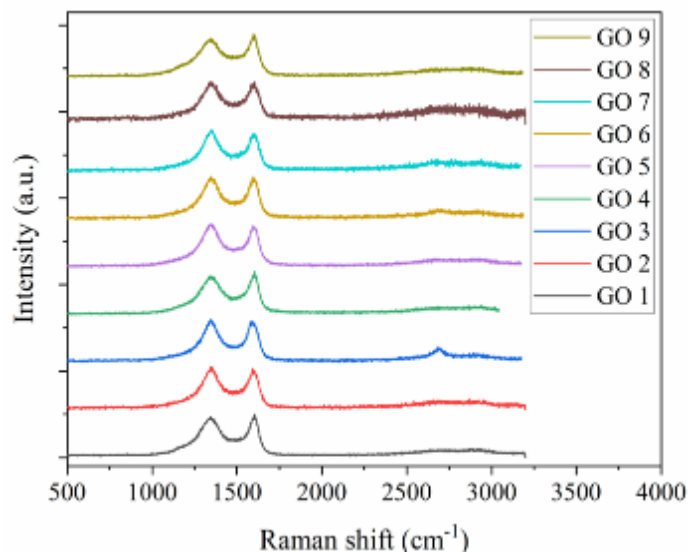


Figure 24. Raman spectra of the 9 graphene oxide samples synthesized under different Taguchi conditions.

4.3.1.2 Multi-Response Optimization Using Grey Relational Analysis

Because no single experimental condition simultaneously optimized oxygen functionalization and structural preservation, Grey Relational Analysis (GRA) was employed to identify the most balanced graphene oxide precursor condition within the investigated design space.

Unlike conventional larger-the-better optimization approaches, the O/C ratio was treated using a nominal-the-best criterion because both insufficient and excessive oxidation are undesirable for graphene oxide intended for subsequent reduction and supercapacitor applications. Excessively low O/C values indicate incomplete oxidation and limited exfoliation, whereas excessively high O/C values are associated with irreversible disruption of the sp^2 carbon framework and poor conductivity recovery after reduction [77, 159]. Based on literature-reported oxidation windows for reducible graphene oxide systems, an O/C target value of approximately 0.55 was selected as

the desired oxidation state [77, 156]. Raman I_D/I_G ratio was treated using the smaller-the-better criterion to minimize excessive structural disorder [152, 153].

Following normalization, Grey Relational Coefficients (GRCs) were calculated for both responses, and the overall Grey Relational Grade (GRG) was determined using weighting factors of 0.60 and 0.40 assigned to O/C and I_D/I_G ratio, respectively. The higher weighting assigned to O/C reflects the importance of achieving sufficient oxygen functionalization for exfoliation and controlled reduction, while Raman disorder was treated as a secondary but still critical parameter governing structural preservation. The resulting GRG-based analysis is summarized in Figure 25b, showing both the main effects plots for mean GRG and the ranking of all experimental runs. The calculated GRG values identified Run 1 as the optimum synthesis condition within the investigated parameter space. The optimization results are summarized in Table 22.

Table 22: Grey Relational Grades and ranking of GO synthesis conditions

Run	O/C	I_D/I_G	GRG	Rank
1	0.55	0.94	0.879	1
4	0.43	0.89	0.855	2
5	0.48	1.05	0.673	3
2	0.38	1.04	0.586	4
6	0.85	0.99	0.568	5
9	1.30	0.90	0.548	6
8	1.04	1.01	0.456	7
3	0.16	1.06	0.456	8
7	1.12	1.12	0.371	9

The optimum synthesis condition corresponded to:

- KMnO₄ dosage: 5 g
- Acid ratio: 3
- Oxidation temperature: 40 °C

- Oxidation time: 6 h

Under these conditions, the synthesized graphene oxide achieved an O/C ratio of 0.55 and a Raman I_D/I_G ratio ratio of 0.94, indicating a balanced structure containing sufficient oxygen functionality while maintaining substantial graphitic integrity.

The optimization results further demonstrate that excessively aggressive oxidation conditions were detrimental to overall GO quality. Although Runs 7–9 achieved substantially higher O/C values, these samples also exhibited elevated disorder and likely excessive disruption of the conjugated carbon network [151, 152].

Overall, the GRA approach successfully identified an oxidation window capable of balancing oxygen functionalization and structural preservation, thereby producing a graphene oxide precursor suitable for subsequent reduction and electrochemical applications [77, 156].

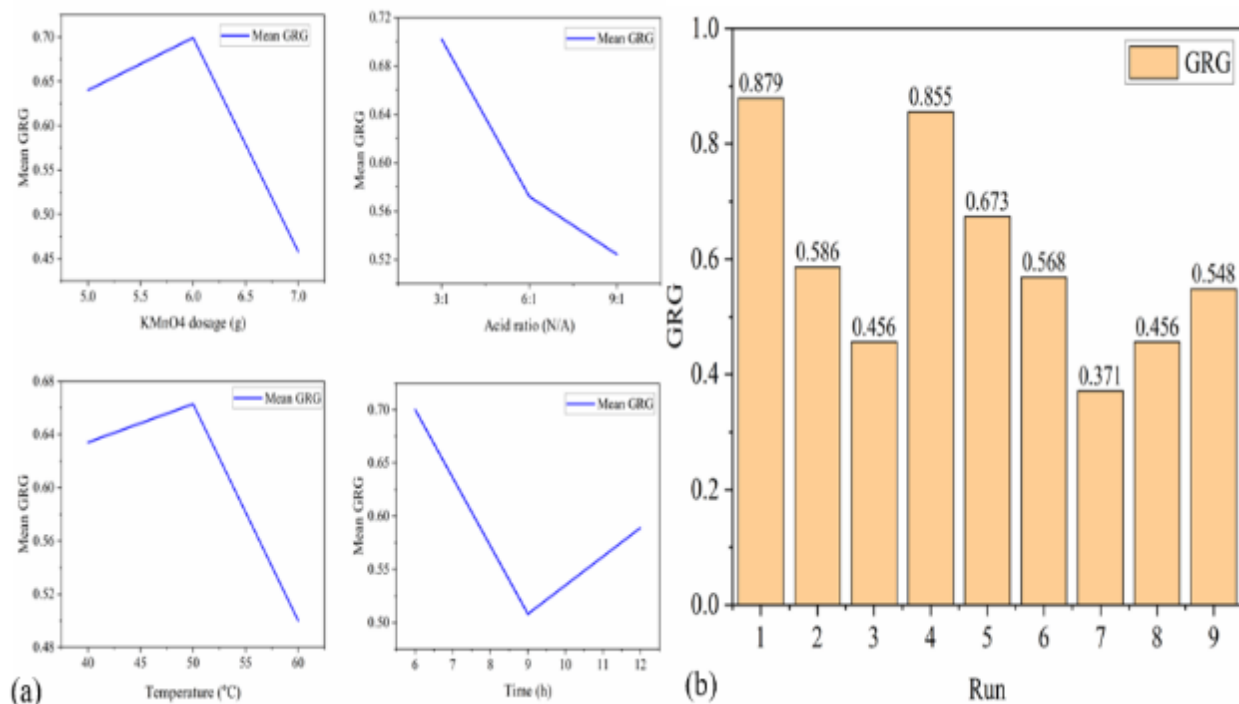


Figure 25. Optimization summary showing (a) main effects plots for mean GRG and (b) Grey Relational Grade ranking across all GO synthesis runs.

4.3.1.3 Effect of Individual Oxidation Parameters

The main effects analysis revealed that all investigated oxidation parameters influenced graphene oxide formation, although their relative contributions differed substantially.

KMnO₄ dosage exhibited the strongest influence on oxidation degree. Increasing oxidant loading generally increased the O/C ratio, indicating enhanced oxygen incorporation into the graphitic framework [157]. However, excessive oxidant concentration also promoted higher Raman disorder, suggesting progressive disruption of the sp² carbon lattice [152, 154].

The acid ratio also strongly affected GO formation. Higher acid ratios promoted more aggressive oxidation and increased oxygen functionalization [157, 158], although excessively acidic conditions produced highly oxygen-enriched structures that may contain unstable or non-ideal oxygen environments [150]. On the other hand, the oxidation temperature significantly influenced structural evolution. Moderate temperatures promoted controlled oxidation, whereas higher temperatures accelerated oxidative attack on graphitic domains, resulting in increased structural disorder and excessive oxygen incorporation [154, 155]. Furthermore, oxidation time showed a similar trend. Shorter reaction durations favored partial oxidation and graphitic preservation, while prolonged oxidation promoted increasingly defective oxygen-rich structures [151].

Collectively, these results demonstrate that graphene oxide formation depended strongly on balancing oxidation intensity and structural preservation. Moderate oxidation conditions produced the most chemically balanced graphene oxide structures for subsequent reduction applications [77, 156, 157].

4.3.1.4 Selection of the Optimized GO Sample

Based on the combined Taguchi–GRA optimization results, Run 1 was selected as the optimum graphene oxide synthesis condition and designated as GO-OPT.

The optimized synthesis parameters consisted of:

- KMnO_4 dosage: 5 g
- Acid ratio: 3
- Oxidation temperature: 40 °C
- Oxidation time: 6 h

Under these conditions, the synthesized GO exhibited:

- O/C ratio of 0.55
- Raman I_D/I_G ratio of 0.94

These values indicate successful formation of a moderately oxidized graphene oxide structure containing sufficient oxygen functional groups for exfoliation and subsequent reduction while maintaining substantial graphitic ordering.

The structural and compositional characteristics of GO-OPT are discussed in the following section.

4.3.2. Structural and Compositional Characterization of GO and rGO Derivatives

4.3.2.1. Structural and Chemical Evolution of GO-OPT and B-GO

Following the selection of GO-OPT from the Taguchi–GRA analysis, the structural and chemical characteristics of the optimized Tour-derived GO were compared with the boric acid-assisted

oxidation product (B-GO) to examine how different oxidation environments influence the transformation of biographite into oxidized carbon materials.

Raman spectroscopy, X-ray diffraction (XRD), FTIR spectroscopy, thermogravimetric analysis (TGA), and FE-SEM/EDS were used to evaluate the comparative behavior of the two oxidation routes to understand changes in graphitic ordering, surface chemistry, thermal stability, and elemental composition.

The Raman spectra (Figure 26a) of B-GO and GO-OPT both exhibit the characteristic D and G bands of oxidized carbon [18, 62], with I_D/I_G ratio values of 0.90 and 0.94, respectively. The similarity of these ratios indicates that both oxidation routes generated highly defective carbon frameworks containing substantial disruption of the sp^2 lattice [40, 142]. The slightly higher I_D/I_G ratio of GO-OPT suggests a marginally greater degree of oxidation-induced disorder, although the difference between the two materials is relatively small.

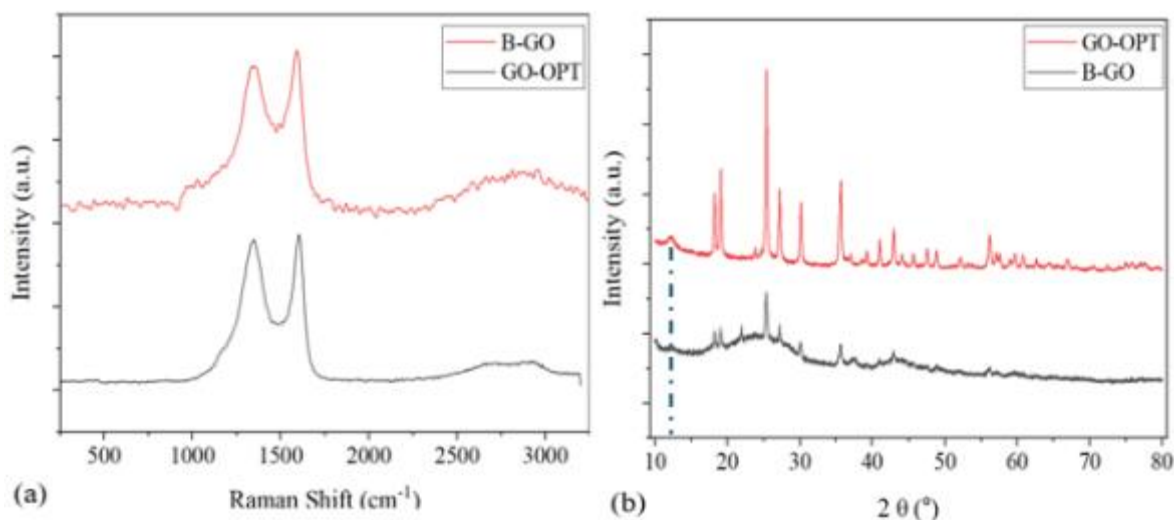


Figure 26. Raman spectra (a), and the XRD pattern (b) showing the secondary peaks and the characteristic peak of GO in both GO-OPT and B-GO.

When examining the XRD patterns as exhibited in Figure 26b, some notable differences become apparent. The B-GO sample mainly shows broad, low-intensity peaks, with a diffuse reflection

around 24–26°. This feature is typical of carbon materials with a largely disordered, turbostratic structure after oxidation [138, 140]. On the other hand, GO-OPT reveals a clear low-angle peak near 11–12°, which is generally associated with an increased spacing between layers—likely due to the introduction of oxygen-containing groups during oxidation [62, 150]. Interestingly, in both samples, several sharp peaks are also observed between 18° and 60°. These additional reflections do not match the expected pattern for graphene oxide [62, 151]. Instead, they point to the presence of crystalline inorganic phases embedded within the oxidized carbon framework. This suggests that the conditions used during oxidation may have either encouraged the formation of these secondary phases or preserved existing ones alongside the GO structure, such as encapsulated Fe in the starting biographite, catalyzing side reactions, especially during the quenching of the oxidation with H₂O₂.

The differences observed by XRD become more apparent when the thermal behavior and surface chemistry of both materials are examined through TGA and FTIR analysis (Figure 27).

When studying the TGA results for B-GO and GO-OPT, both samples show the usual pattern you get with oxidized carbons: a rapid weight drop at lower temperatures was initially observed, which is likely water and some loosely held volatile species that were being released [77, 153]. After that, the weight loss progressed slowly, and this could be due to the breakdown of oxygen groups and the gradual loss of the carbon backbone [69, 77]. This stepwise loss is typical for materials like graphene oxide [77], but it's remarkable to see how closely both samples follow this trend. The high level of weight retention is connected to testing in an N₂ atmosphere, which reduces material loss. The presence of manganese and phosphate-related species that are more resistant to temperature is likely another contributing factor. Despite these similarities, GO-OPT consistently retains a greater proportion of its mass throughout the heating cycle and exhibits a higher residual

weight at 800 °C than B-GO. This behavior could be due to the presence of a larger thermally stable fraction in GO-OPT, which is consistent with the additional crystalline components observed in its XRD pattern.

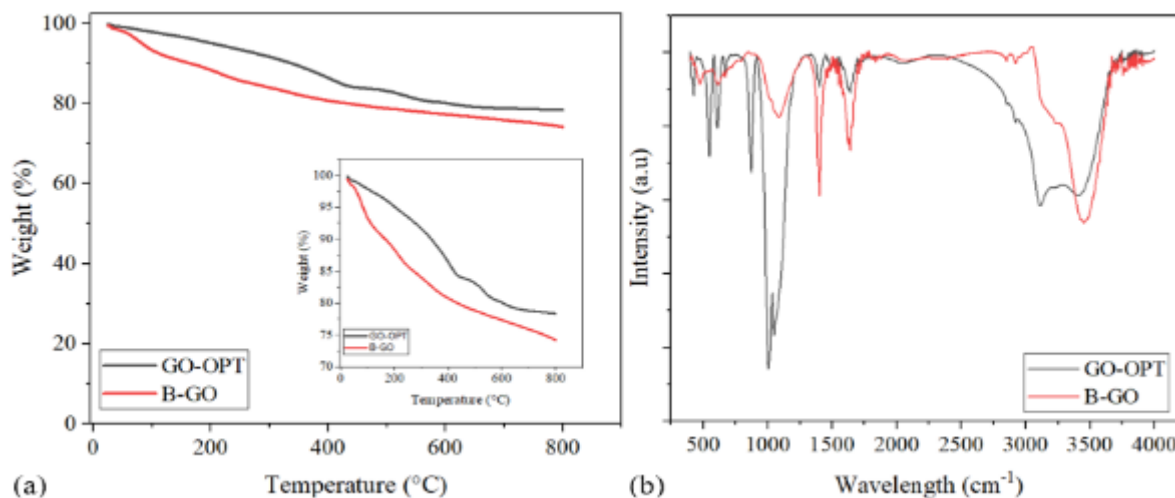


Figure 27. (a) Thermogram (TGA) and (b) FTIR spectra of both GO samples

The FTIR spectra provide further insight into the chemical functionalities present in both materials. B-GO and GO-OPT display broad O–H stretching vibrations between 3100 and 3400 cm^{-1} , together with absorptions near 1630–1650 cm^{-1} , and within the 1000–1100 cm^{-1} region, corresponding to oxygen-containing groups commonly associated with graphene oxide structures [62, 153]. Weak bands around 2860 and 2920 cm^{-1} further indicate the presence of residual aliphatic carbon species [153]. Both oxidation methods produced FTIR spectra that appear quite similar, which suggests that they introduced roughly the same species of oxygen groups to the carbon structure. Still, FTIR does not show much difference in the actual surface groups between the samples. On the other hand, the TGA data paint a different picture: there are clear differences in how the materials behave when heated and in the amount of non-volatile residue left behind. This points to real variations in the thermal stability and composition that FTIR alone doesn't detect.

Going further, the scanning electron microscope (SEM) images (Figure 28 a and c) show clear differences in the appearance of the products made using the two oxidation methods. GO-OPT appears rough and uneven, with clusters of tiny particles packed closely together. In contrast, B-GO looks smoother and more granular, with fewer visible particles on its surface. The patchy, varied texture of GO-OPT matches what is seen in its XRD pattern, indicating that the sample contains more than just oxidized carbon.

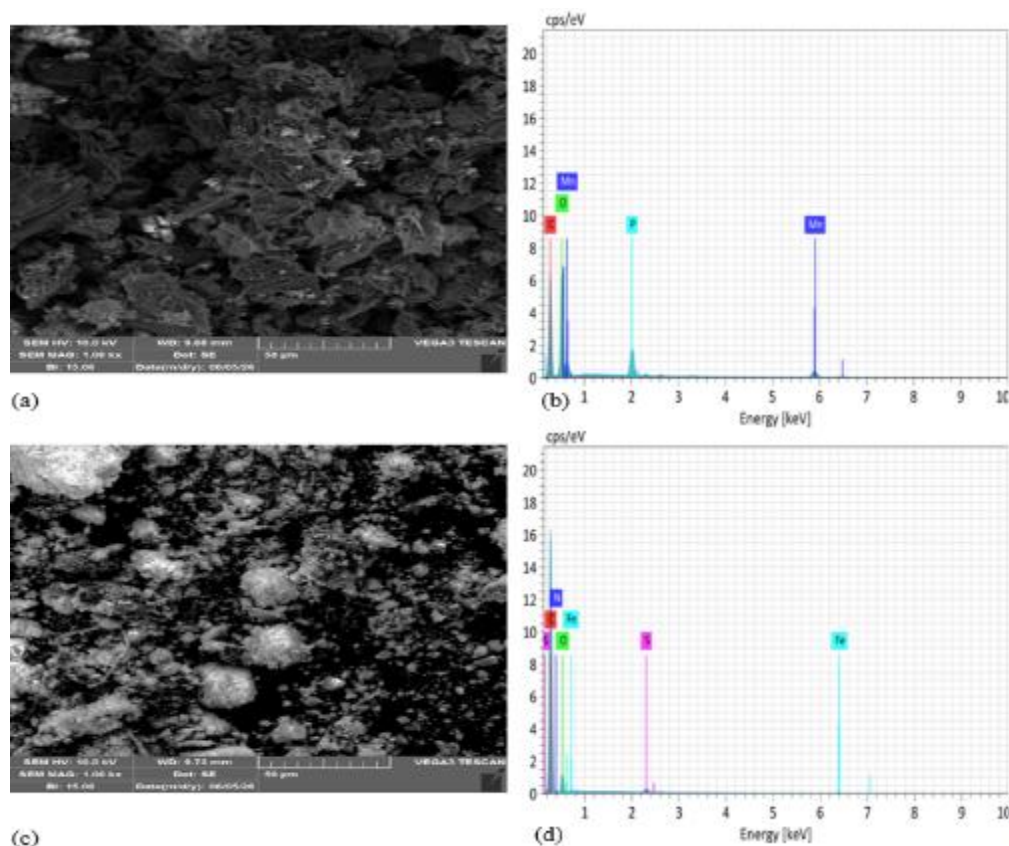


Figure 28: SEM micrographs (a, c) and corresponding EDX spectra (b, d) of GO-OPT and B-GO

Energy-dispersive X-ray (EDX) analysis also shows clear differences between the two samples (Figure 28b and d, and Table 23). GO-OPT has almost equal amounts of carbon and oxygen, with a good amount of manganese and phosphorus as well. Detecting both manganese and phosphorus at these levels aligns with the XRD results, showing that GO-OPT contains more than just carbon;

it also has crystalline inorganic materials formed during oxidation. This could explain why GO-OPT leaves behind more residue when assessed with TGA.

Table 23. Elemental composition of GO-OPT and B-GO determined by EDX analysis

Element	GO-OPT (EDS b) Atom %	B-GO (EDS d) Atom %
Carbon K	43.57	83.71
Oxygen K	43.39	13.26
Manganese K	8.52	1.41
Phosphorus K	4.52	0.24
Chlorine K	N/A	N/A
Iron K	N/A	0.68
Sulfur K	N/A	0.51
Potassium K	N/A	0.25

B-GO, on the other hand, is made up mostly of carbon, with much less oxygen. Only tiny amounts of manganese, iron, sulfur, potassium, and chlorine were found. Nitrogen showed up in the EDX scan, but it was not measured precisely because EDX is not great at picking up light elements. No phosphorus was detected, and the manganese content was much lower. This suggests that using boric acid did not lead to the creation or preservation of the manganese- and phosphorus-rich inorganic particles seen in GO-OPT. Instead, B-GO stayed mostly carbon-based, matching its broader XRD results and the smaller amount of leftover material in TGA tests.

The comparative characterization of GO-OPT and B-GO shows that the oxidation environment strongly influences the structure and composition of the resulting oxidized carbon materials [150, 151]. While both samples exhibit defect-rich oxidized carbon features from Raman and comparable oxygen-containing functionalities from FTIR, the XRD, TGA, and EDX analyses reveal clear differences between the two products. GO-OPT displays a more clearly defined GO-like layered structure but also contains significant Mn- and P-associated inorganic components, which account for its higher thermal residue. In contrast, B-GO exhibits a predominantly carbon-

rich composition, lower oxygen incorporation, and a more turbostratic structure [62, 138, 140, 151].

Based on all the analyzed data, the characteristics of B-GO suggest a partial reduction-like behavior during the oxidation process [77, 160]. This could be linked to the interactions between the oxidation environment and residual catalytic species within the carbon framework [23, 151]. However, confirming this mechanism would amount to performing further surface chemical analysis. Based on the combined structural and compositional results, GO-OPT was selected as the precursor for the subsequent reduction study, where the influence of different reduction pathways on oxygen removal, defect evolution, and structural reconstruction is examined.

4.3.3. Reduction of GO-OPT using Different Reduction Pathways

GO-OPT, prepared using the Tour method, was reduced to evaluate its usefulness as an electrode in a supercapacitor. As described in the methodology, three reduction routes were used in this research—chemically reduced GO (CrGO), thermally reduced GO (TrGO), and sequentially reduced GO (CTrGO). The produced rGOs were examined using Raman spectroscopy, XRD, SEM/EDX, XPS, and TGA. These routes impose different chemical and thermal environments, and each produces a distinct balance between defect generation, oxygen removal, and structural reorganization [77, 160] as discussed next.

4.3.3.1. Structural and Chemical Evolution of The Explored Reduction Pathways

Raman spectroscopy as shown in Figure 29a provides the clearest initial indication of how the carbon lattice responds to each reduction method. GO exhibits an I_D/I_G ratio of 0.90, reflecting a highly oxidized and disordered framework. Chemical reduction increases this ratio to 1.09,

showing that oxygen removal alone does not restore graphitic order; instead, it exposes pre-existing defects and generates new ones as oxygen groups detach [159, 161]. Thermal reduction produces a different outcome: TrGO shows an I_D/I_G ratio of 1.04, suggesting partial reorganization of sp^2 domains under higher thermal energy [69, 77]. Sequential reduction (CTrGO) combined ascorbic acid treatment with mild thermal annealing at 400 °C for 60 min. This sample exhibited an I_D/I_G ratio of 1.08, like CrGO, indicating that the low-temperature thermal step was not enough to repair the defect-rich configuration created by chemical reduction [69, 70, 161]. These results show that while chemical reduction effectively removes oxygen, only high-temperature thermal treatment (700 °C) achieves significant structural repair. The sequential pathway with a 400 °C anneal does not outperform thermal reduction alone.

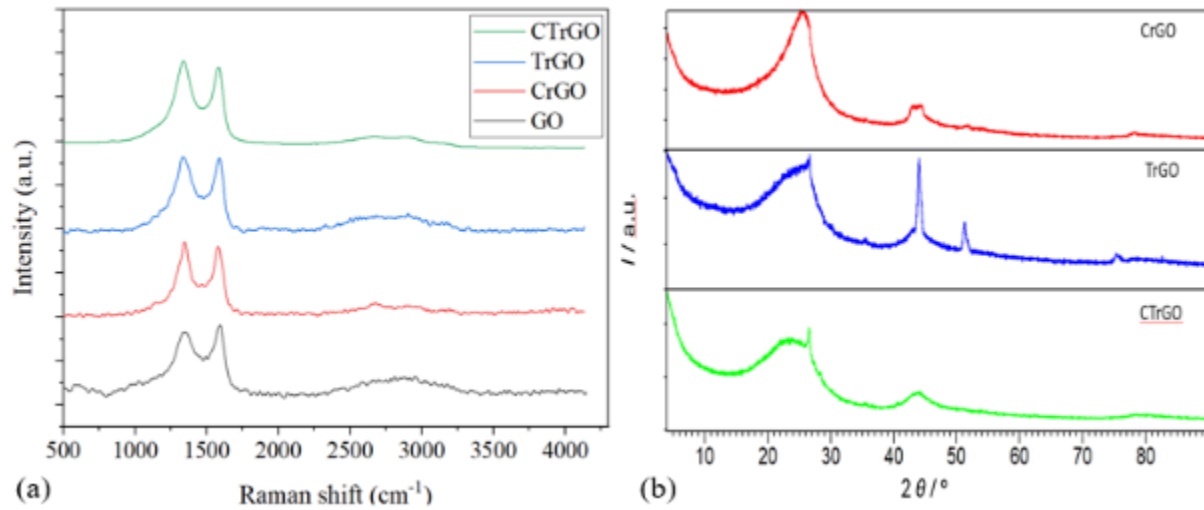


Figure 29. Raman spectra (a) and XRD patterns of the rGOs derived from GO-OPT.

The XRD patterns reinforce the structural trends already suggested by Raman analysis. Referring back to the GO pattern shown earlier in Figure 29b, where the 001 reflection of GO-OPT appeared around 11-12°, the reduced samples display the expected signatures of turbostratic disorder and expanded interlayer spacing.

Table 24. Defect densities (I_D/I_G) and using different reduction routes

Sample	I_D/I_G	I_{2D}/I_G
CrGO	1.09	Broad
CTrGO	1.04	Broad
CTrGO	1.08	Broad

In CrGO, this spacing partially collapses, and the (002) feature shifts toward 25° , but the peak remains broad, indicating that chemical reduction alone does not promote meaningful restacking [160, 161]. However, TrGO shows a noticeably sharper, more intense (002) peak at around 26.1° , accompanied by a distinct 100 reflection at 44° [69, 77]. This suggests that some degree of in-plane ordering and partial graphitic reconstruction has taken place. A weaker peak near 50.1° is also seen, suggesting a minor secondary crystalline phase that becomes more apparent upon thermal treatment. CTrGO sits between these two extremes: its (002) peak is more defined than in CrGO but still broader than in TrGO, and the additional reflections are less pronounced, implying that the defect structure introduced during chemical reduction limits the extent of thermally driven reorganization [67, 162]. Put together, the Raman and XRD results show that chemical deoxygenation and structural graphitization do not proceed in lockstep but instead follow partially independent pathways [52, 77, 160].

In the earlier analysis, the GO-OPT and B-GO samples were analyzed using a TESCAN SEM paired with a BRUKER EDX. The reduced derivatives were analyzed with an FE-SEM (JEOL JSM-7000F) paired with an Oxford INCA EDX. Because different equipment was used, the absolute elemental percentages from these datasets are not directly comparable. Instead, the SEM–EDX results shown in Figure 30 are considered by looking at the elemental trends within each analysis set and how they correspond to structural changes identified by Raman and XRD.

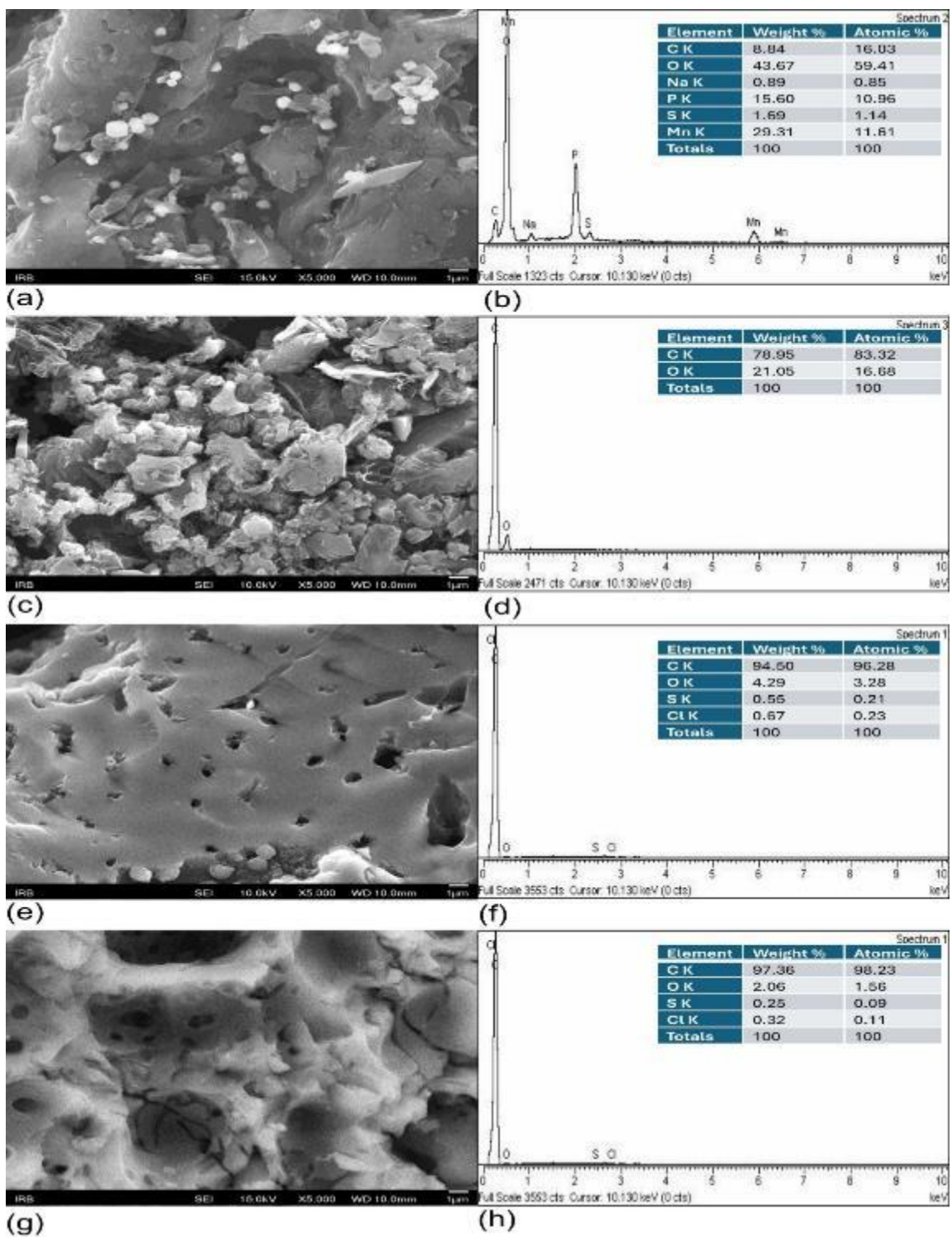


Figure 30. Morphological features and Elemental Composition of GO-OPT (a, b), CrGO (c, d), TrGO (e, f), and CTrGO (g, h).

The analysis data gathered from SEM and EDX provide complementary insight into morphological and elemental evolution [77, 153]. GO-OPT displayed a heterogeneous, aggregated morphology containing embedded Mn–phosphate-derived inorganic phases which could be from synthesis route [163, 164]. EDX confirms the presence of significant Mn, P, and oxygen contributions, suggesting that oxidation was accompanied by the formation and retention of inorganic species within the GO matrix [164]. This supports the XRD observations, where additional crystalline reflections were attributed to Mn-containing inorganic phases rather than the carbon framework itself. The presence of these phases is consistent with the possibility that residual Fe-containing catalytic sites inherited from the graphitized precursor influenced the oxidation environment by promoting partial reduction of manganese species during oxidation [16, 133].

After chemical reduction, CrGO (Figure 30c) transforms into exfoliated, wrinkled sheets with significantly higher carbon content. Mn and P signals disappear, confirming that chemical reduction and acid washing destabilize and remove the inorganic phase [52, 65, 66, 160]. This indicates that the Mn–phosphate-derived species are not strongly retained within the reduced carbon framework and can be removed during the chemical treatment stage. Thermal reduction yields a more continuous carbon framework with smoother texture [69], while CTrGO (Figure 30g) exhibits similar morphology but with higher chemical purity. Across all reduced samples, Mn and P are absent in EDX spectra, demonstrating that their removal occurs during the chemical reduction stage rather than during thermal treatment [67, 159].

TEM analysis, as shown in Figure 31, further illustrates the morphological differences produced by the different reduction routes. The TEM image of GO-OPT in Figure 31a shows a dense and highly aggregated structure dominated by high-contrast inorganic domains, which obscure the

underlying carbon framework and make distinct sheet-like regions difficult to resolve. After chemical reduction with ascorbic acid (Figure 30b, CrGO), thinner and more extended sheet-like structures become visible, with relatively transparent regions in the lower part and a thicker, heavily crumpled multilayered fold at the top. TrGO (Figure 31c) shows a more compact and corrugated structure, with darker overlapping regions and stronger folding, suggesting greater stacking or compaction of the carbon layers following the 700 °C treatment. The combined treatment (CTrGO) produces more extended and semi-transparent sheet regions with moderate wrinkling (Figure 31d), giving a morphology that falls between CrGO and TrGO.

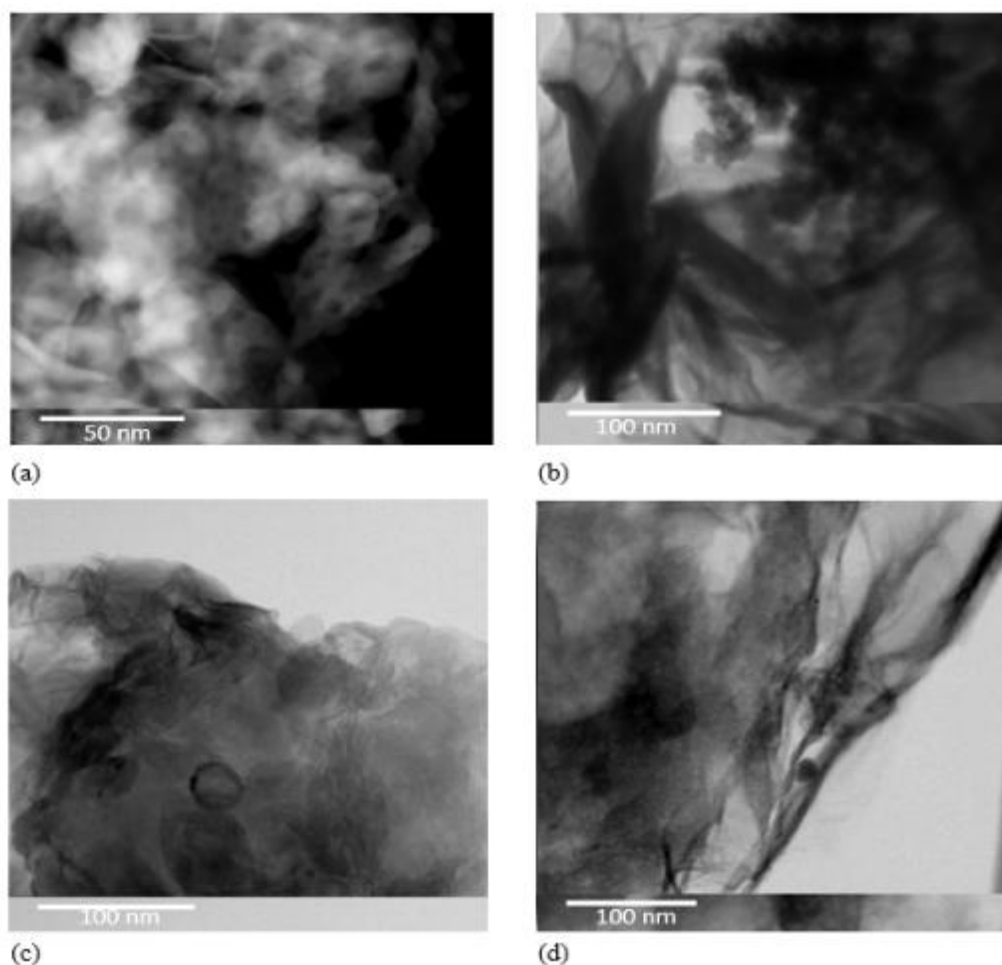


Figure 31. TEM images of GO and reduced GO samples: (a) contaminated GO, (b) CrGO, (c) TrGO, and (d) CTrGO.

These morphological differences complement the Raman results, showing that changes in sheet morphology and the degree of graphitic ordering do not necessarily follow the same trend across the reduction routes.

XPS further clarifies the evolution of surface chemistry. This is shown in Figure 32. GO is dominated by oxygenated carbon species (C–O, C=O, O–C=O), consistent with its low structural order. CrGO shows substantial removal of these functionalities but an increase in defect-related carbon environments, aligning with its elevated I_D/I_G ratio [159, 161]. TrGO exhibits a more balanced distribution of C–O and C=O species, reflecting partial restoration of sp^2 domains [69, 77, 165]. CTrGO contains the lowest oxygen content, confirming the highest reduction efficiency among the samples. Importantly, Mn and P species are absent in all reduced samples, supporting the conclusion that inorganic removal is driven by chemical reduction and acid washing [162, 165].

These findings enable a direct comparison of the three reduction strategies. Chemical reduction is highly effective at removing oxygen and dissolving inorganic phases but is limited in defect recovery and conductivity restoration due to the exposure of defects during deoxygenation [52, 162, 166]. Thermal reduction is not only efficient at removing oxygen but also substantially enhances structural order and electrical continuity through partial graphitic reconstruction [69, 70]. Sequential reduction achieves the highest chemical purity and complete inorganic removal; however, its defect structure remains largely unchanged relative to the chemical step, which could limit improvements in conductivity and structural recovery. From an electrochemical perspective, CrGO offers a high surface area but exhibits poor charge transport; TrGO demonstrates superior performance due to enhanced sp^2 connectivity, and CTrGO represents an intermediate case, being chemically pure but structurally limited [65, 77, 156].

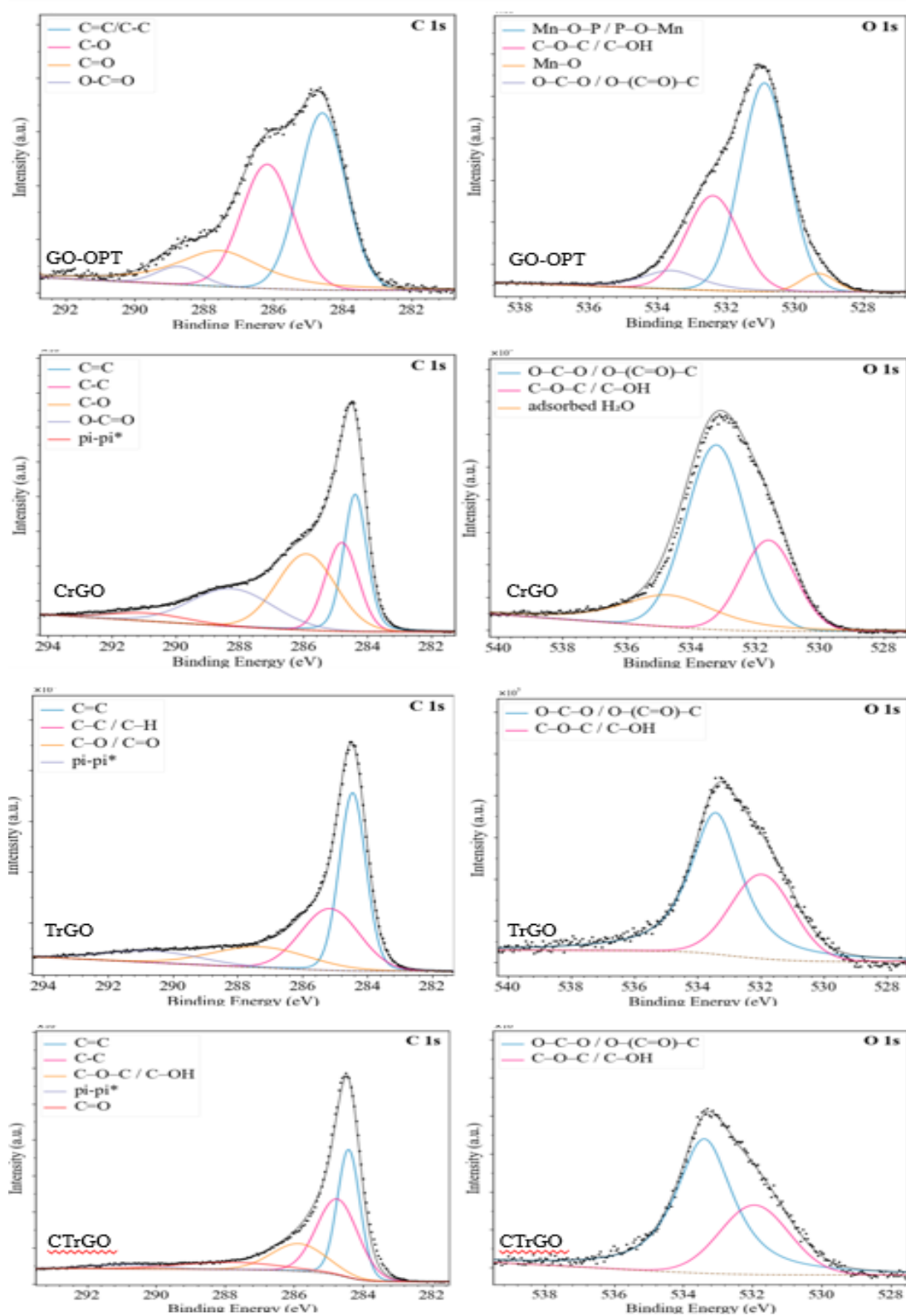


Figure 32. C 1s and O 1s of GO-OPT and the reduced graphene oxides from the applied reduction routes.

4.3.3.2. Reduction Mechanism and Structural Evolution

The combined characterization data support a two-stage, partially decoupled reduction mechanism, as depicted in Figure 33.

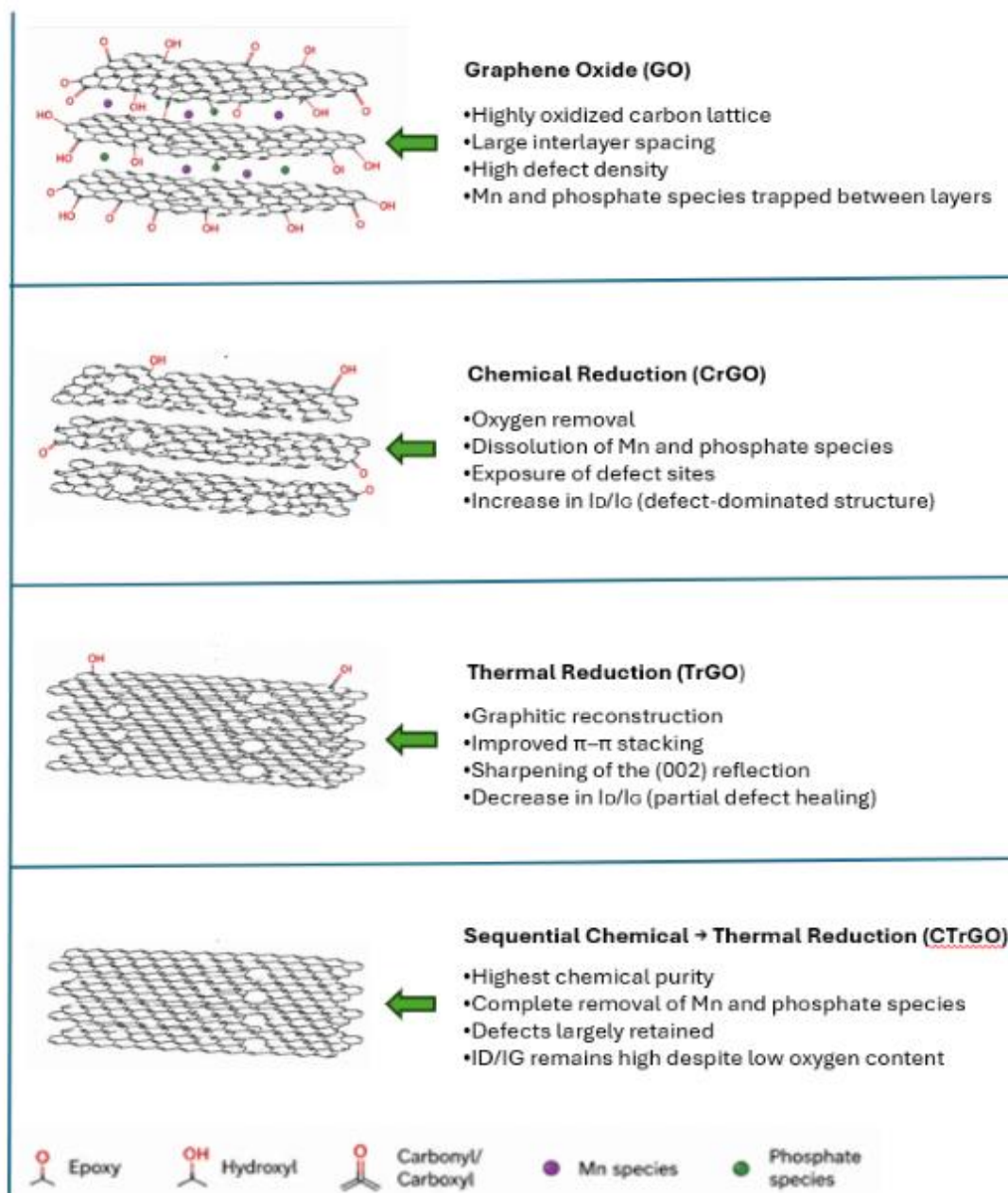


Figure 33: Schematic illustration of the structural and chemical evolution of graphene oxide (GO) during chemical, thermal, and sequential chemical–thermal reduction. The diagram highlights oxygen removal, Mn/P dissolution, defect exposure, partial graphitic reconstruction, and the differing extents of defect recovery and ordering achieved in CrGO, TrGO, and CTrGO.

In the initial stage, chemical reduction removes oxygen-containing functional groups and destabilizes manganese-phosphate inclusions, yielding a chemically cleaner yet defect-rich carbon framework [67, 160]. The subsequent stage involves thermal energy, which promotes partial graphitic reconstruction and enhances the continuity and stacking of sp^2 domains [69]. In the sequential reduction route, the chemical step establishes a defect-rich configuration that subsequent thermal treatment cannot fully reorganize [67, 70]. This observation explains the lack of direct correlation between oxygen removal and Raman disorder, and indicates that structural ordering in reduced graphene oxide is primarily governed by thermal energy rather than deoxygenation alone [156].

The combined characterization results demonstrate that the transformation from GO-OPT to rGO involves more than simple oxygen removal. Chemical reduction primarily promotes deoxygenation and removal of oxidation-derived inorganic species, whereas thermal treatment provides the energy required for partial restoration of sp^2 carbon domains and improved structural connectivity. The differences observed among CrGO, TrGO, and CTrGO in terms of defect density, graphitic ordering, morphology, and chemical composition are expected to influence charge transport and ion accessibility. The resulting electrochemical behavior of these materials is therefore discussed in the following section

4.3.3.3. Electrochemical Diagnostic Probe using Supercapacitor

In addition to the structural, functional and morphological analysis, the electrochemical behaviour of the samples changes quite noticeably after reduction, although the overall performance remains limited in organic electrolyte systems due to restricted ion transport and higher interfacial resistance [4, 54]. All materials show clear capacitive characteristics, but the extent of charge storage varies with how the structure and chemistry evolve during reduction [7, 53]. The cyclic

voltammograms in Figure 34a show capacitive behaviour for all three materials, with CrGO giving the largest enclosed area, followed by TrGO and then CTrGO. This reflects CrGO's comparatively higher charge-storage response among the samples.

From the GCD results as shown in Figure 34b, CrGO ranks as the material with the highest specific capacitance (25.63 F g^{-1}). CTrGO follows with 4.74 F g^{-1} , while TrGO sits slightly lower at 11.63 F g^{-1} . The values obtained from CV show the same overall trend, although they are consistently higher, which is not unusual because the CV technique frequently captures additional surface and fast charge contributions that are not fully expressed under constant current discharge [5, 55].

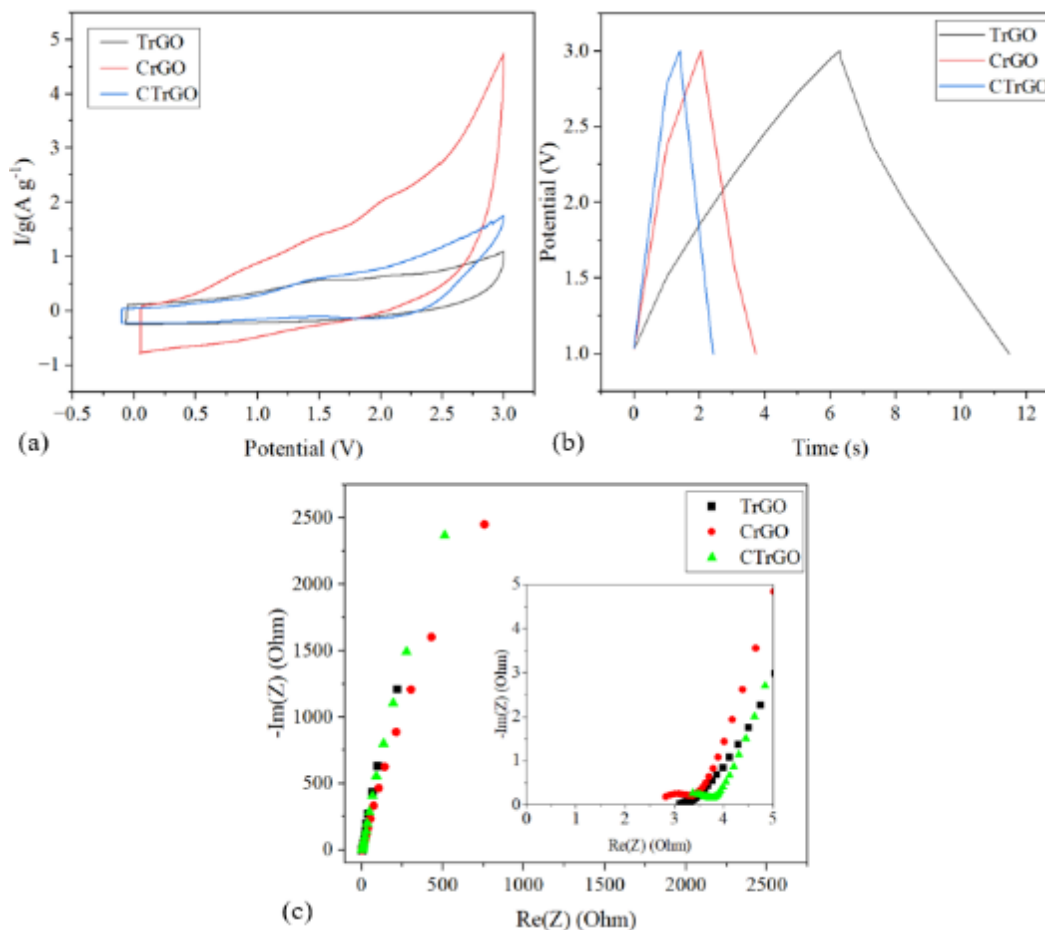


Figure 34: Electrochemical characterization of CrGO, TrGO, and CTrGO using (a) cyclic voltammetry, (b) galvanostatic charge–discharge, and (c) Nyquist plots from electrochemical impedance spectroscopy.

Interestingly, the “best” sample in terms of structural order (TrGO) is not the best sample electrochemically. It performs poorly despite improved graphitic ordering, indicating that improved conductivity alone does not translate into higher capacitance in organic electrolyte systems. CrGO performs better overall despite higher disorder, suggesting that accessible surface sites and defect-related charge storage dominate in this case [167]. CTrGO is the weakest performer, and this is a consistent trend across both CV and GCD. Its higher ESR ($3.37\ \Omega$) suggests that sequential treatment resulted in poorer charge transfer and insufficient restoration of conductive pathways. In addition, the structural disorder introduced during chemical reduction, which appeared to persist even after thermal annealing, could be behind the limited electron transport continuity observed.

Within the studied reduction series, CTrGO occupies a distinct position, representing the combined outcome of sequential chemical and thermal processing, in which oxygen removal is maximized while structural reconstruction remains limited. This makes it a useful reference point for understanding how chemical deoxygenation and thermal reorganization do not necessarily proceed in a coupled manner in reduced graphene materials.

Looking at the ESR values in Table 25 revealed an interesting trend. Lower resistance tends to correlate with higher capacitance, particularly for CrGO compared to CTrGO. This reinforces the idea that ion and electron transport capability is just as important as surface chemistry in determining performance in organic electrolyte systems [5-7].

Table 25. Electrochemical performance of rGO derivatives (CrGO, TrGO, CTrGO) in organic electrolyte

Sample	CV ($C_s / F\ g^{-1}$)	GCD ($C_s / F\ g^{-1}$)	ESR (Ω)
TrGO	13.54	11.63	3.10
CrGO	39.48	25.63	2.83
CTrGO	29.20	4.74	3.37

Overall, the results suggest that electrochemical performance does not depend on a single structural parameter. Instead, charge storage is governed by a balance between accessible surface area, defect concentration, and conductive network continuity.

4.4. Heteroatom Doping

4.4.1. Hydrothermal Doping

4.4.1.1. Response Variability and Strategic Success of the Hydrothermal Doping Approach

The variation in structural and compositional-related responses across the hydrothermal design matrix is illustrated by the Raman spectra in Figure 35. The measured responses are summarized in Table 26. These results show that the hydrothermal thiourea treatment substantially affected both the carbon framework and heteroatom incorporation of the graphene-like carbon precursor.

Table 26. L9 orthogonal array experimental design and measured responses for hydrothermally doped graphene-like carbon samples.

Sample	Thiourea dosage (g)	Temperature (°C)	Time (h)	I_D/I_G	N (%)	S (%)
HD-GLC1	2	160	6	0.76	0.072	0.088
HD-GLC2	2	180	12	1.00	0.067	0.067
HD-GLC3	2	200	24	0.08	0.076	0.072
HD-GLC4	3	160	12	1.00	0.079	0.089
HD-GLC5	3	180	24	0.62	0.091	0.072
HD-GLC6	3	200	6	0.20	0.090	0.080
HD-GLC7	4	160	24	0.54	0.096	0.085
HD-GLC8	4	180	6	0.95	0.083	0.074
HD-GLC9	4	200	12	0.37	0.095	0.074

The parent SA-GLC exhibited an I_D/I_G ratio of about 0.95. This indicates a highly defective turbostratic carbon structure [168]. After hydrothermal treatment, the I_D/I_G ratio ranged from 0.08 to 1.00. This suggests that process parameters greatly influenced the carbon framework's structural

change. Nitrogen and sulfur contents also varied, from 0.067–0.096% and 0.067–0.089%, respectively. doped graphene-like carbon samples.

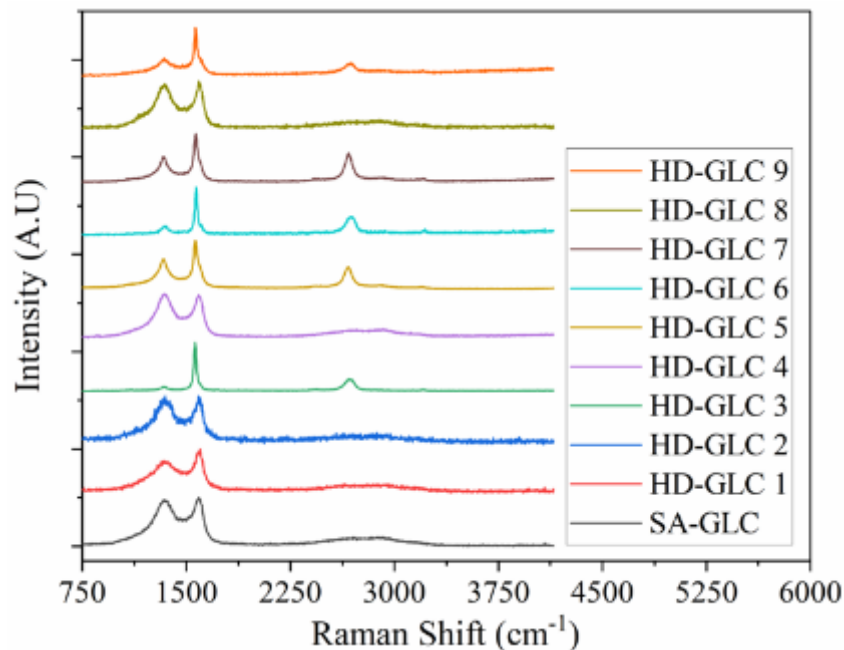


Figure 35. Raman spectra of the 9 doped samples from the Taguchi design

Observing Table 26 and Figure 35, several notable trends are identified. HD-GLC 3 had the lowest I_D/I_G ratio (0.08); this indicates extensive structural reconstruction when compared to the parent material. In contrast, HD-GLC4 and HD-GLC2 retained I_D/I_G values close to unity, so structural disorder remained dominant under those hydrothermal conditions. HD-GLC7 had the highest nitrogen content (0.096%). HD-GLC4 showed the highest sulfur content (0.089%). No single sample maximized all measured responses, showing the process's complexity. Conditions that increased graphitic ordering did not always yield the highest heteroatom contents. Samples with higher nitrogen or sulfur were not always the least disordered. This divergence indicates that hydrothermal treatment involves competing processes: carbon framework reconstruction, defect generation, and heteroatom incorporation. These processes may operate with different intensities under each combination of temperature, time, and thiourea dosage.

The broad response range across the L9 array confirms that the hydrothermal strategy effectively modifies the parent SA-GLC. This variation, as discussed in the methodological chapter, is essential for finding meaningful structure–property relationships. More importantly, it highlights the need for a multi-objective optimization approach that balances structural ordering and chemical functionalization. Therefore, Grey Relational Analysis (GRA) was used to identify the optimal hydrothermal conditions.

4.4.1.2. Dual Optimization and Visual Justification via Grey Relational Analysis (GRA)

Grey Relational Analysis was used to find the hydrothermal condition that best balanced structural order and heteroatom incorporation. The optimization considered three responses: Raman I_D/I_G ratio, nitrogen content, and sulfur content. Because lower structural disorder is desirable, I_D/I_G used the Smaller-the-Better criterion. Nitrogen and sulfur contents were normalized using the Larger-the-Better criterion [169, 170]. Weightings were set to 0.4 for I_D/I_G and to 0.3 for both nitrogen and sulfur, indicating the need to preserve graphitic order while improving surface functionality for supercapacitor use[171]. This weighting scheme, though simple, creates a slight bias toward structural restoration. Keep this in mind as the results are discussed. The GRG result is revealed in Table 27 and Figure 36.

Examining the ranking shows something important: the optimum sample did not have the lowest I_D/I_G ratio. HD-GLC3 had excellent structural ordering ($I_D/I_G = 0.08$) but only moderate nitrogen and sulfur contents. This limited its ranking. In contrast, HD-GLC7 had the highest nitrogen content (0.096%) and high sulfur retention (0.085%), while also exhibiting improved structural order relative to the parent SA-GLC. This trade-off, not a single maximized response, led to the best GRG. This finding fits with the dataset’s main theme: hydrothermal modification seldom optimizes one property without sacrificing another.

Table 27. Grey Relational Analysis results for hydrothermally doped graphene-like carbon samples. (Using $I_D/I_G = 0.4$, $N = 0.3$, $S = 0.3$)

Sample	GRG	Rank
HD-GLC7	0.720	1
HD-GLC6	0.694	2
HD-GLC9	0.653	3
HD-GLC3	0.644	4
HD-GLC5	0.618	5
HD-GLC4	0.576	6
HD-GLC1	0.521	7
HD-GLC8	0.457	8
HD-GLC2	0.333	9

Among the tested conditions, HD-GLC7 had the highest GRG (0.720). HD-GLC6 followed with 0.694, and HD-GLC9 had 0.653. HD-GLC2 showed the lowest GRG (0.333), meaning poor overall performance. The results echo an earlier point: the relationship between structural order and heteroatom incorporation rarely aligns perfectly, as reinforced by the GRA.

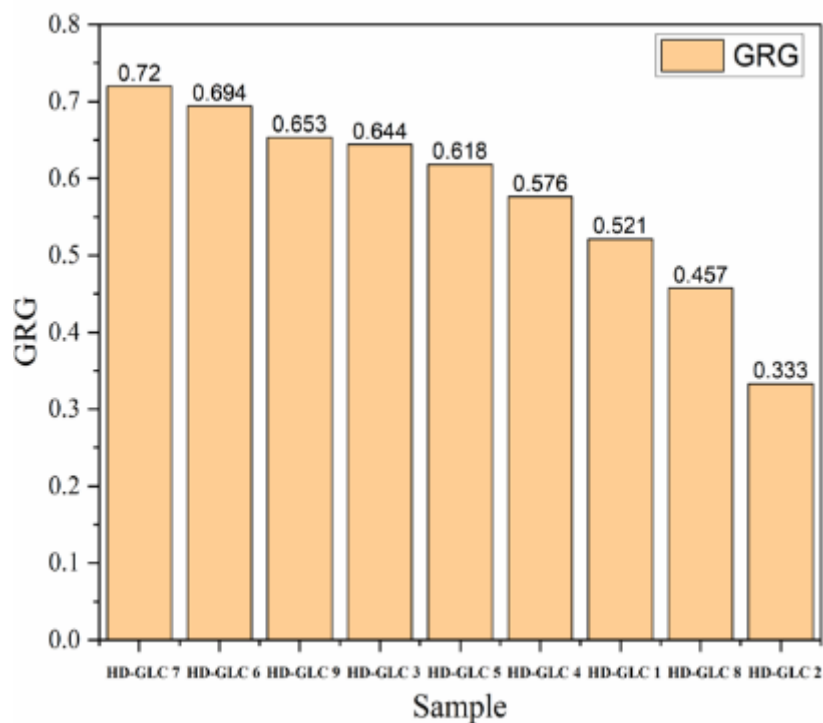


Figure 36. Grey relational grades and ranking of the hydrothermal doping experiments.

These results show GRA's value in resolving competing objectives that cannot be judged by single response parameters. The method does not eliminate trade-offs but provides a structured way to weigh them. The analysis also suggests that successful hydrothermal modification needs simultaneous attention to both structural and chemical aspects, especially for electrochemical energy storage use. This dual-objective view, while sometimes overlooked, grows more important as the material moves from lab characterization to practical integration.

4.4.1.3. Factor Influence and Mechanistic Interpretation Supported by ANOVA

The effects of thiourea dosage, hydrothermal temperature, and reaction time on the overall response were analyzed with analysis of variance (ANOVA) on the grey relational grade. Table 28 presents the results, and Figure 37 shows the main effects plot. At this point, the statistical trends echo qualitative patterns noted earlier, but ANOVA gives a more formal way to interpret them.

Table 28. ANOVA results for grey relational grade (GRG).

Factor	DOF	Sum of Squares	Contribution (%)
Thiourea dosage	2	0.01585	12.15
Temperature	2	0.09326	71.49
Time	2	0.01909	14.64
Error	2	0.00224	1.72
Total	8	0.13045	100.00

Temperature was the dominant factor, accounting for 71.49% of total GRG variation. Reaction time and thiourea dosage contributed 14.64% and 12.15%, respectively. This result is consistent with general understanding and substantiates the idea that the hydrothermal process depends mainly on thermally induced changes in the carbon framework, not just on precursor concentration [43]. Temperature likely drives both defect formation and heteroatom incorporation in the carbon

materials [83, 172]. The other variables modulate these effects rather than controlling them outright. The general impact of the hydrothermal synthesis factors is illustrated in the Figure below.

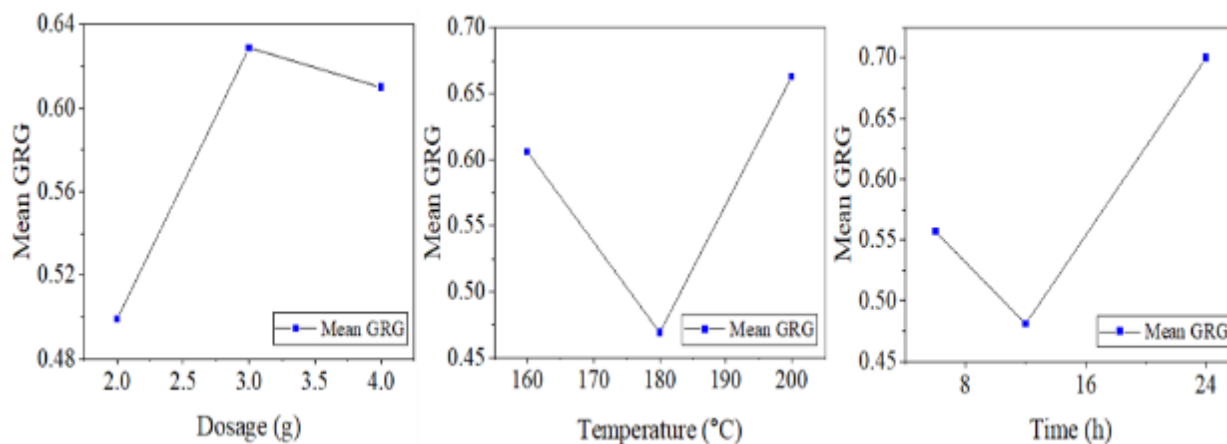


Figure 37. Main effects plot showing the influence of process variables on mean grey relational grade.

However, the response does not show a simple monotonic trend. The average GRG at 180 °C was lower than at 160 or 200 °C. This suggests a transitional hydrothermal regime. At this stage, thiourea decomposition and defect generation become important, while carbon reconstruction continues [80]. As a result, structural ordering, nitrogen incorporation, and sulfur retention are all compromised. This subtle intermediate behavior hints at a balance between competing reaction pathways. At 200 °C, the system shifts toward a reconstruction-dominated regime. Samples from this temperature had much lower average I_D/I_G values and better nitrogen incorporation. This may mean that more mobile carbon fragments and increased interaction with thiourea decomposition products aid the restoration of partial graphitic order while retaining nitrogen functionalities. Still, this result does not mean the structure fully recovers; rather, it suggests a better compromise between ordering and doping.

Focusing on 160 °C, this temperature favored sulfur retention, yielding the top-ranked sample, HD-GLC7. As discussed earlier, the optimum condition did not come from maximizing structural

order alone, but from balancing graphitic reconstruction with heteroatom preservation. This agrees with the GRA results and shows that hydrothermal treatment acts as both a doping and a structural modification strategy.

Overall, these observations show that the process is multi-dimensional and that no single parameter works alone.

4.4.1.4. Structural and Compositional Characterization of Selected Samples

To understand the structural origins of the hydrothermal modification states identified by Raman spectroscopy and GRA, three representative samples — HD-GLC3, HD-GLC5, and HD-GLC7 — were selected for further examination. Looking at these samples in detail helps clarify the underlying structures that the earlier statistical trends only hint at.

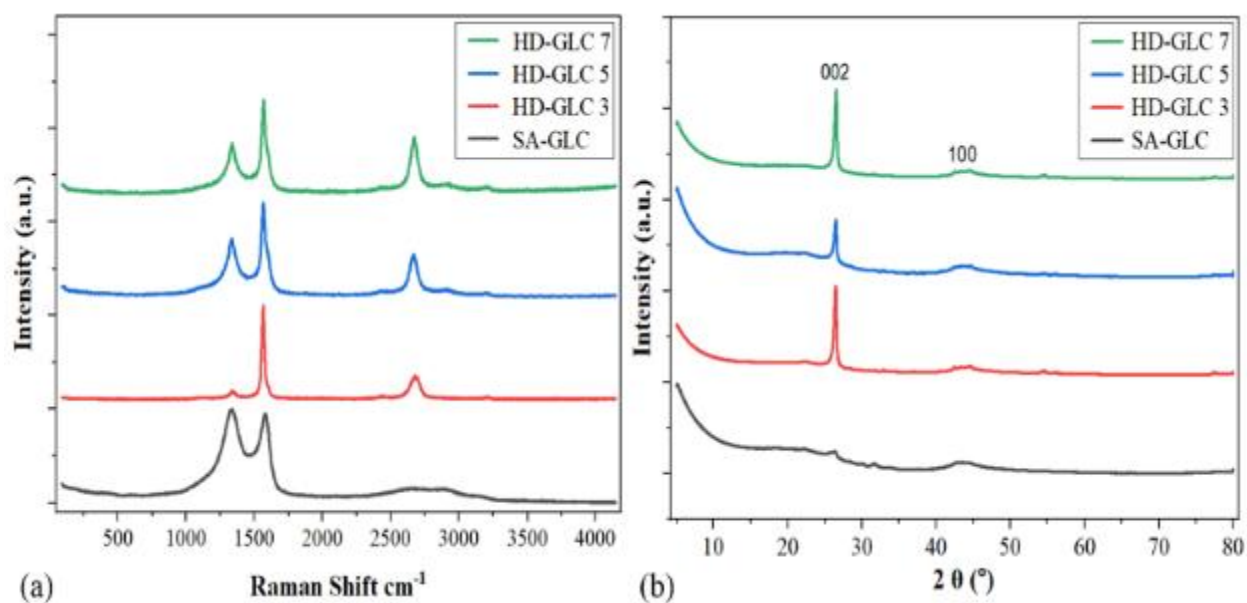


Figure 38. Raman and X-ray diffraction analysis of selected hydrothermally doped graphene-like carbon samples.

In Figure 38, the combined Raman and XRD results are shown and analyzed. Consistent with its exceptionally low I_D/I_G ratio, HD-GLC3 exhibited the highest degree of structural ordering among

the selected samples. A distinct (002) reflection appeared, with a calculated d_{002} spacing of 3.372 Å. This confirms substantial graphitic reconstruction compared to the turbostratic parent SA-GLC. The corresponding crystallite dimensions ($L_c = 20.9$ nm and $L_a = 240$ nm) further support the development of larger, more ordered graphitic domains [123, 140]. This reconstruction likely shows a temperature-driven reorganization of carbon layers [13, 140], as was suggested earlier.

Table 29. Raman and XRD derived structural metrics for the doped samples.

Sample	I_D/I_G	I_{2D}/I_G	L_a (nm)	d_{002}	L_c (nm)	N_{sheet}	Degree of G (%)
HD-GLC3	0.08	0.25	240	0.3375	21.2	64	76
HD-GLC5	0.62	0.45	31	0.3371	20.7	62	80
HD-GLC7	0.54	0.61	36	0.3366	21.3	64	86

The morphological and elemental characteristics extracted from SEM and EDX analyses are shown in Figure 39. It can be seen that HD-GLC3 exhibited a comparatively smooth and continuous carbon matrix (Figure 39c), whereas HD-GLC5 (Figure 39e) displayed localized surface disruption and bright crystalline inclusions. When the figure is analyzed further, HD-GLC7 (Figure 39g) exhibited the greatest structural heterogeneity, comprising dense carbon regions interspersed with porous, sheet-like features.

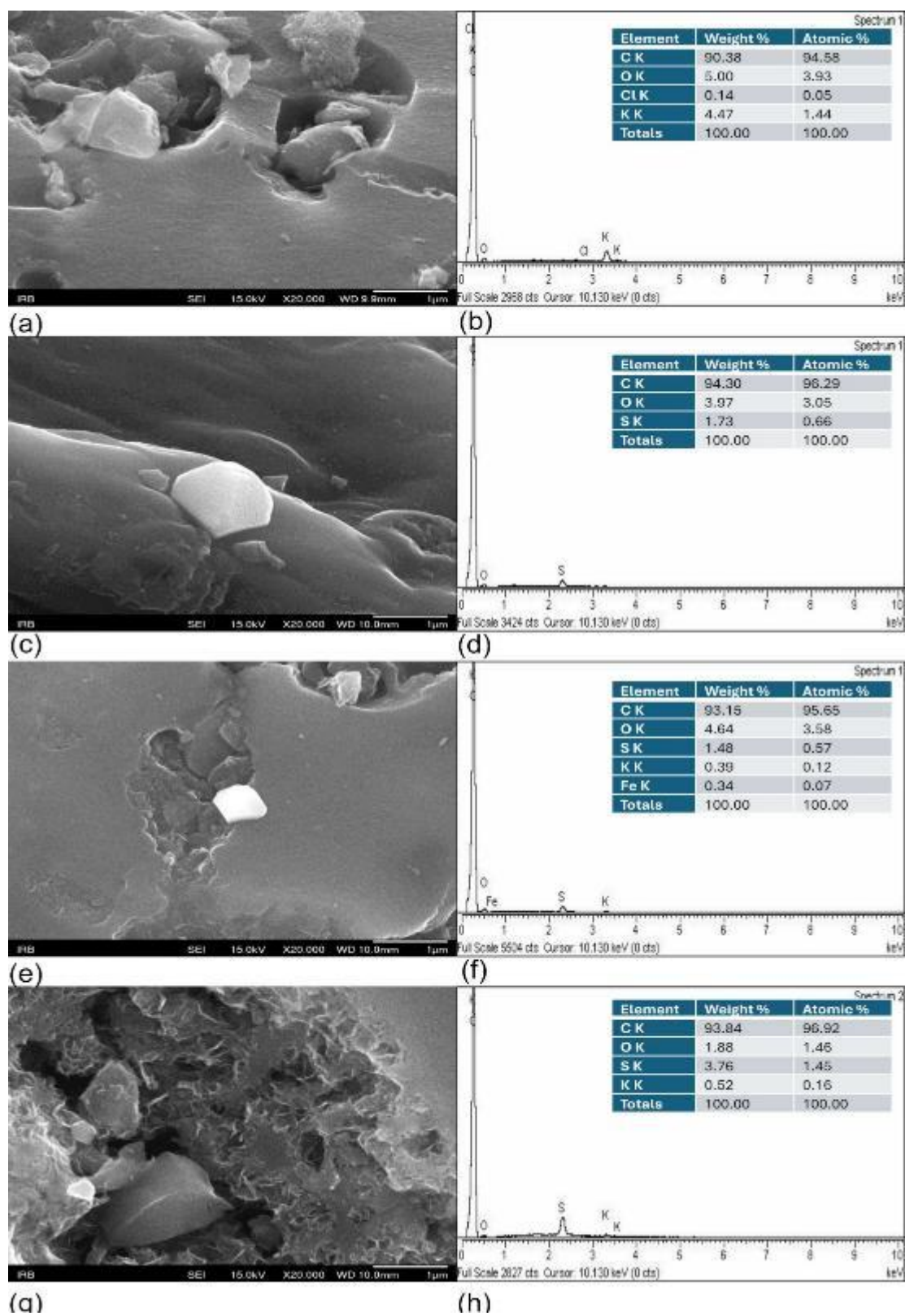


Figure 39. SEM micrographs and EDX spectra of HD-GLC3, HD-GLC5, and HD-GLC7.

EDX detected sulfur in all samples, with the highest level in HD-GLC7 — consistent with the CHNS results. Nitrogen was not detected due to EDX's limited sensitivity to light elements. This combination of morphological irregularity and elevated sulfur content suggests that the lower temperature regime retains certain thiourea-derived functionalities — functionalities that are otherwise diminished at higher temperatures.

XPS analysis (Figure 40) reveals that graphitic carbon is the main component in the C 1s spectra for all samples, pointing to the retention of the sp^2 carbon framework after hydrothermal treatment. Nitrogen appears mostly as pyridinic and pyrrolic forms within the carbon structure, with HD-GLC7 showing the highest amount of pyridinic nitrogen. Sulfur is found mainly as thiophenic sulfur, indicating it has become part of the aromatic carbon network rather than merely attaching to the surface [173]. The small differences in the intensities of these species from sample to sample suggest subtle variations in how these atoms are bonded locally—details that bulk elemental analysis may miss.

Table 30 below summarizes all the environmental states of the carbon, oxygen, nitrogen, and sulfur components of the hydrothermally doped samples. This includes the O 1s in the appendix of this work.

Table 30. Summary of XPS Peak Assignments for Selected Hydrothermally Doped Samples

Sample	C 1s	N 1s	S 2p	O 1s
HD-GLC 3	Graphitic carbon (sp^2), defect carbon	Pyridinic N, pyrrolic N	Thiophenic sulfur	C–O, C=O, Fe–O
HD-GLC 5	Graphitic carbon (sp^2), defect carbon, heteroatom-bound carbon	Pyridinic N, pyrrolic N	Thiophenic sulfur	C–O, C=O, Fe–O
HD-GLC 7	Graphitic carbon (sp^2), heteroatom-bound carbon	Pyridinic N (dominant), pyrrolic N	Thiophenic sulfur	C–O, C=O, Fe–O

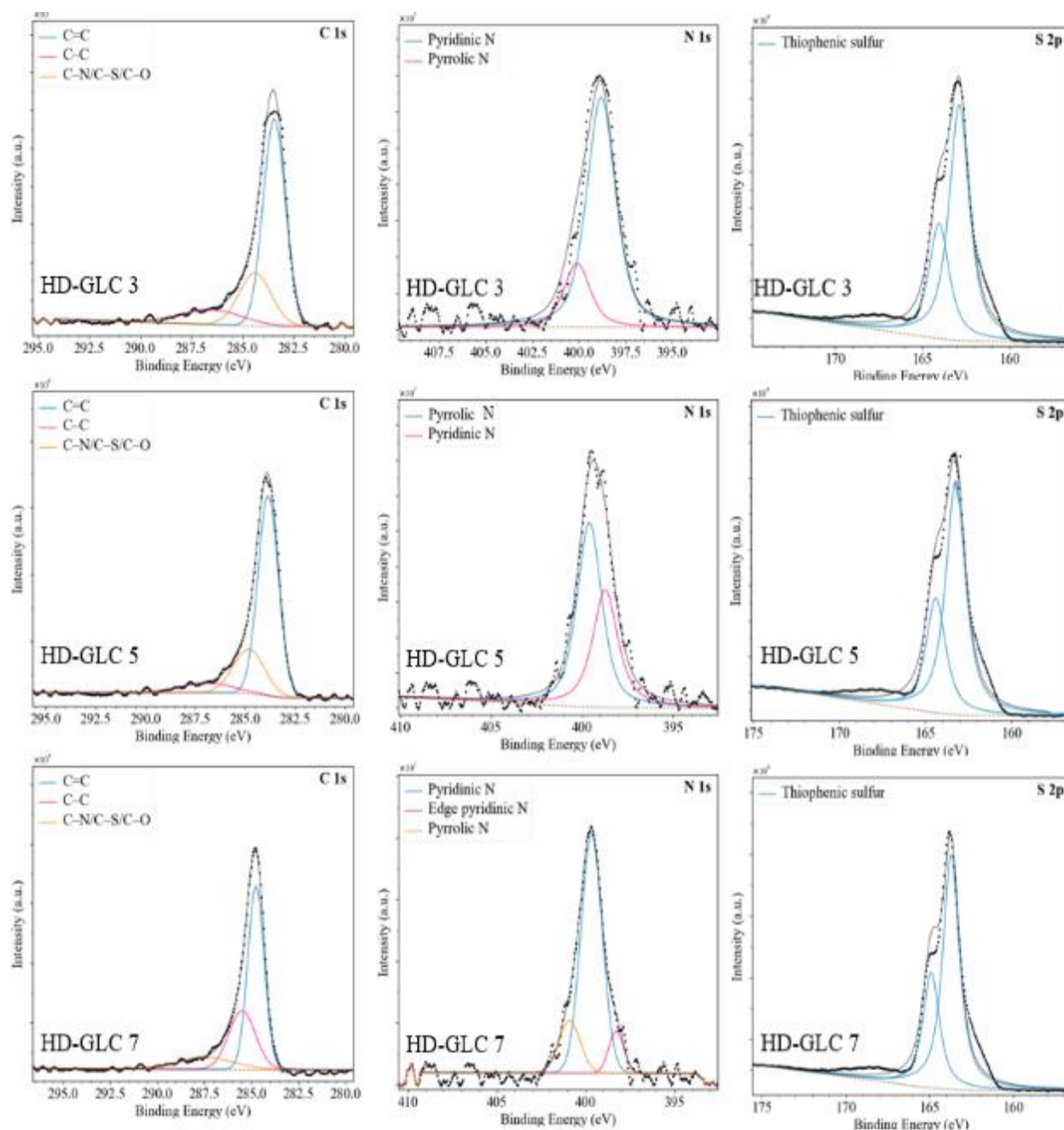


Figure 40. High-resolution XPS spectra of C 1s, N 1s and S 2p regions for selected hydrothermally doped graphene-like carbon samples.

Thermogravimetric analysis (TGA) was used to compare the thermal stability of heteroatom-doped GLC samples with an undoped SA-GLC reference. Analyzing Figure 41, each sample showed gradual, multi-stage weight loss as the temperature increased to 800 °C, which is typical for carbon-based materials that contain surface groups and doped heteroatoms. The first weight loss,

which occurred below 150 °C, came from water and loosely attached volatile compounds leaving the sample. Later weight losses reflected the breakdown of oxygen-related surface groups, heteroatom-linked features, and the gradual decomposition of the main carbon structure at higher temperatures [4, 54].

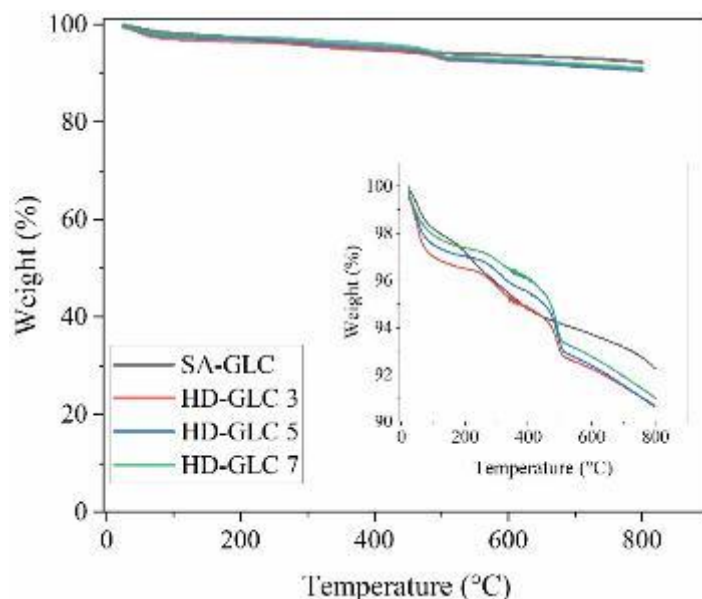


Figure 41. Thermogravimetric analysis of SA-GLC and hydrothermally doped HD-GLC samples.

All samples lost weight in a similar manner as they decompose, but a closer look shows some small differences between SA-GLC and the hydrothermally doped HD-GLC3–HD-GLC7 samples. The doped samples retained slightly more weight and left a bit more residue, which suggests that the hydrothermal process changed how heat affected the carbon. These changes are consistent with those observed in other tests, such as Raman, XPS, XRD, and SEM/EDX. Still, the differences are minor, so doping mainly affects the surface and defects, rather than the basic heat resistance of the carbon [134, 135].

Looking at all the data from Raman, XRD, SEM/EDX, and XPS, three distinct types of hydrothermal modification become clear, just as described by the Taguchi-GRA framework.

HD-GLC3 mainly shows signs of reconstruction, with a tightly ordered graphitic structure. HD-GLC5 falls between reconstruction and functionalization, showing a mix of both features. HD-GLC7 is notable for having a high content of pyridinic nitrogen and thiophenic sulfur, yet it retains its graphitic regions. This unique blend of structure and elements is likely why HD-GLC7 scored the highest grey relational grade, making it the top material among those tested. All in all, hydrothermal modification seems to rely on several overlapping mechanisms, each playing a different role depending on how the material is made [16, 48].

4.4.1.5. Electrochemical Analysis Using Supercapacitor

In addition to the structural, functional, and morphological analysis, the electrochemical behaviour of the samples changes quite noticeably after hydrothermal treatment, and the differences are not subtle, as can be seen in Figure 42. All materials exhibit clear capacitive characteristics, but the extent of charge storage varies with how the structure and chemistry evolve during doping [5, 19]. The cyclic voltammograms in Figure 42a show clear capacitive behaviour for all four samples, with the doped materials displaying broader profiles than SA-GLC. Among them, HD-GLC7 produces the largest enclosed area, followed by HD-GLC3, while HD-GLC5 shows a noticeably smaller area. This ordering reflects the relative charge-storage response visible directly from the CV curves.

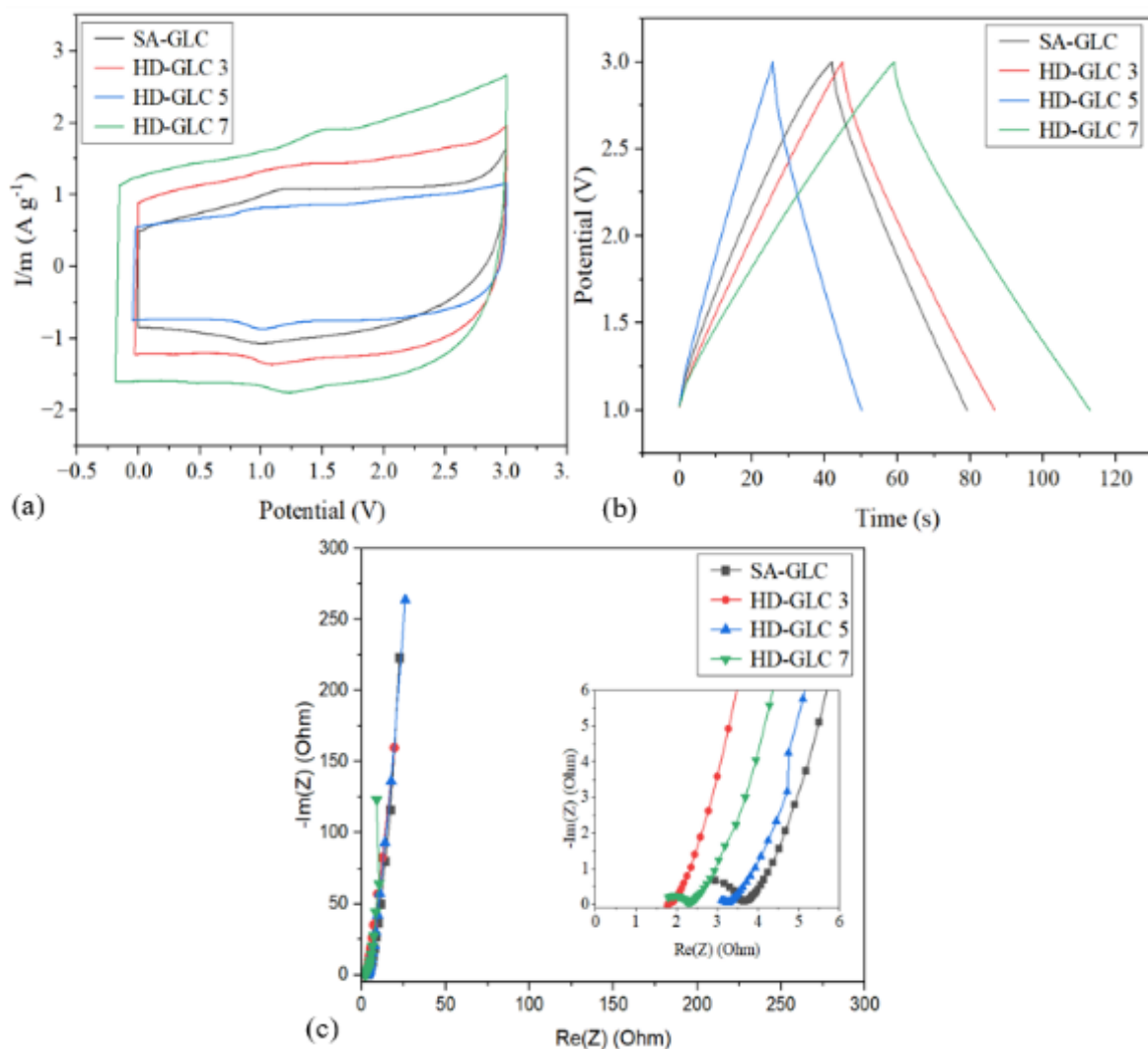


Figure 42. Electrochemical performance evaluation of SA-GLC and heteroatom-doped HD-GLC electrodes: (a) cyclic voltammetry (CV) curves, (b) galvanostatic charge–discharge (GCD) profiles, and (c) electrochemical impedance spectroscopy (Nyquist plots).

From the GCD results, HD-GLC7 ranks as the material with the highest specific capacitance (134.45 F g⁻¹). HD-GLC3 follows with 104.72 F g⁻¹, while SA-GLC sits slightly lower at 92.33 F g⁻¹. HD-GLC5 drops considerably to 60.00 F g⁻¹. The values obtained from the CV show the same overall trend, although they are consistently higher, which is not unusual because the CV technique frequently captures additional surface and fast redox contributions that are not fully expressed under constant current discharge [7].

An interesting observation is that the “best” structural ordering sample (HD-GLC3) is not the best electrochemically. It performed well, but not the best. That role belongs to HD-GLC7. This makes sense when the structural and chemical data are considered together. HD-GLC7 combines relatively low resistance (1.79 Ω) with the highest nitrogen content and strong sulfur retention. So it is not exclusively about having defects or having order — it is about having both conductivity and active chemistry working together [6, 8]. HD-GLC3 tells a slightly different story. It benefits from its more ordered graphitic framework, which helps electron transport, reflected in its low ESR (1.77 Ω). But it does not possess sufficient heteroatom contribution, so its charge storage is more limited compared to HD-GLC7. It is efficient, just not as functionally rich. HD-GLC5 is the weakest performer, and this is quite consistent across all measurements. Its higher ESR (3.11 Ω) suggests poorer charge transfer, and the structural disorder seems to dominate without offering any compensating benefit. In other words, defects alone are not helping here.

Looking at ESR overall (Figure 42c and Table 31), the pattern is quite telling. Lower resistance agrees well with higher capacitance, especially for HD-GLC3 and HD-GLC7. That simple relationship reinforces the idea that ion and electron transport capability is just as important as surface chemistry [20, 53].

Table 31. Specific capacitance (CV and GCD) and equivalent series resistance (ESR) of SA-GLC and hydrothermally doped graphene-like carbon samples.

Sample	CV ($C_s / F g^{-1}$)	GCD ($C_s / F g^{-1}$)	ESR (Ω)
SA-GLC	88.33	92.33	2.95
HD-GLC3	126.17	104.72	1.77
HD-GLC5	77.42	60.00	3.11
HD-GLC7	172.25	134.45	1.79

In conclusion, the results point away from a single “best” structural feature. Rather, performance depends on finding a balance. Too much disorder impairs conductivity, while a high degree of

graphitization reduces the number of active sites. HD-GLC7 sits in that middle space where both effects are present. This is the reason it performs best overall [3, 43].

These results really highlight the importance of controlling the extent of structural modification during chemical functionalization. However, adding heteroatoms is one of the ways of engineering the balance between surface activity and electronic transport—there are other ways to achieve this. The following section analyzes thermal doping as an alternative route, where higher temperatures provide an additional driving force for carbon reorganization and dopant integration.

4.4.2. Thermal-Assisted Heteroatom Doping of Graphitized Carbon

To further investigate the effect of heteroatom incorporation on the synthesized graphitized carbon and its impact on its structure and other properties, a thermal doping method was employed, with thiourea as the source of nitrogen and sulfur. In contrast to the hydrothermal approach, thermal treatment introduces dopants at elevated temperatures, enabling heteroatom incorporation to occur concurrently with structural rearrangement of the carbon framework. The resulting materials were labeled TD-GLC₂, TD-GLC₃, and TD-GLC₄, corresponding to increasing thiourea dosages as described earlier in the methodology.

4.4.2.1. Structural, chemical, and morphological evolution during thermal doping

For the overall analysis of these doped samples, CA-GLC served as the baseline material for thermal doping studies, providing a reference for assessing the impact of thiourea modification on the structural and chemical evolution of the carbon framework.

Raman spectroscopy was first used to evaluate the changes in defect density and graphitic domain structure induced by thermal doping, as observed in Figure 43a. The CA-GLC sample exhibited a moderate defect level with an I_D/I_G ratio of 0.74, an I_{2D}/I_G ratio of 0.35, and an estimated crystallite

size (L_a) of 25.97 nm, indicating the presence of graphene-like carbon domains with partial structural ordering [123].

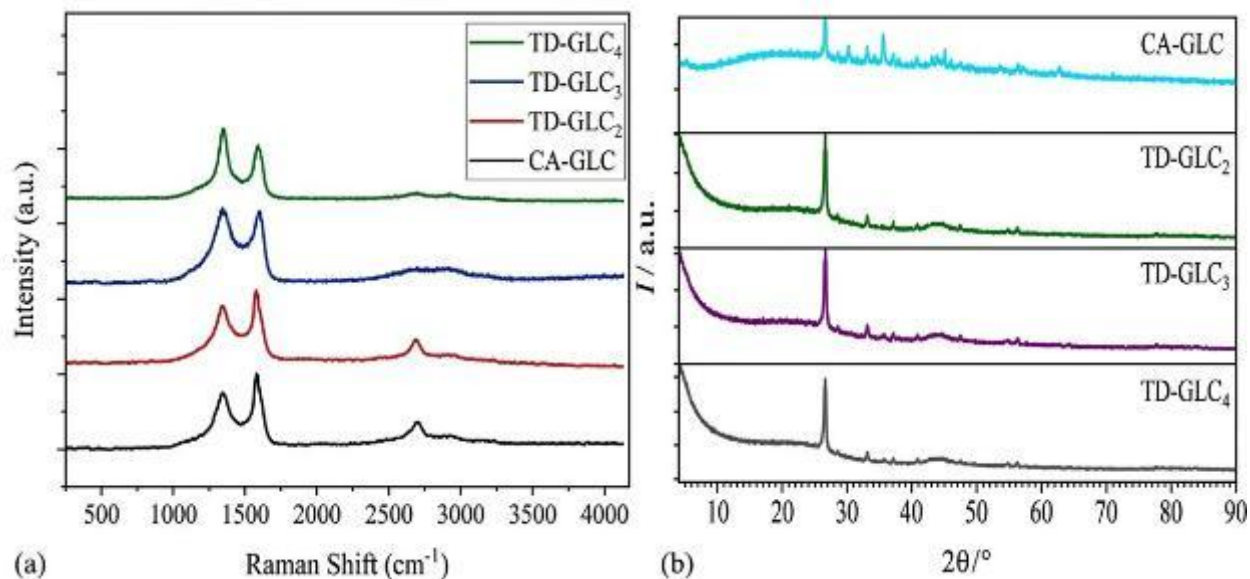


Figure 43. Raman spectra (a) and XRD pattern (b) of the thermally doped graphene-like carbons

Following thermal doping, TD-GLC₂ showed the closest structural similarity to the undoped CA-GLC sample. The I_D/I_G ratio increased only slightly to 0.80, while the I_{2D}/I_G ratio remained unchanged at 0.35, with only a minor reduction in L_a to 24.03 nm. These results indicate that lower thiourea loading enabled heteroatom modification while preserving the existing graphitic framework. Table 32 highlights the data from the Raman analysis.

Increasing the thiourea ratio to 3:1 resulted in a more pronounced structural modification. TD-GLC₃ exhibited an increased I_D/I_G ratio of 1.03 and a broadened I_{2D} feature, suggesting increased defect generation and disruption of graphitic domains [174, 175]. At the highest thiourea loading, TD-GLC₄ showed the greatest structural disorder, with an I_D/I_G ratio of 1.30 and a broadened I_{2D} region accompanied by additional Raman features between approximately 2690–3000 cm⁻¹. These

changes indicate that excessive thiourea promotes extensive surface reactions and defect formation, leading to an increase in the chances of obtaining hierarchical porosity [176].

The Raman results demonstrate that in thermal doping, there is a need to find a balance between introducing chemically active defect sites and maintaining the integrity of the graphitic framework.

The structural trends observed from Raman analysis are further supported by XRD measurements (Figure 43b). The XRD pattern of CA-GLC displayed a sharp (002) reflection around 26.5° , confirming the presence of well-organized graphitic layers generated through KOH activation and iron-assisted graphitization [16, 48]. Weak reflections between 30° and 45° are attributed to residual iron-related crystalline species embedded within the carbon matrix [23].

Table 32. Raman data from the base graphene-like carbon and thermally doped samples.

Sample	I_D/I_G Ratio	I_{2D}/I_G Ratio
CA-GLC	0.74	0.35
TD-GLC ₂	0.80	0.35
TD-GLC ₃	1.03	Broad
TD-GLC ₄	1.30	Broad

After thermal doping, TD-GLC₂ resembled CA-GLC in its XRD pattern. The strong (002) peak around 26.5° was obvious, so most of the graphitic structure remained. But a few of the smaller crystalline reflections visible in CA-GLC faded considerably, which suggests that the thiourea likely modified/transformed some of the leftover crystal bits from the original material. TD-GLC₃ showed a similar graphitic peak, but many of the smaller crystal features were largely gone—so the thiourea showed a greater impact in this system. When the dopant dosage was increased, as in TD-GLC₄, the (002) peak remained significantly high, indicating that the graphitic feature survived the thermal process, but the overall pattern was more defective, even though graphitic features were retained in all samples. The Raman data support this, with a pronounced increase in

the I_D/I_G ratio, indicating that excessive thiourea makes the system much more disordered, even if the backbone remained intact [173, 175].

The thermal stability and surface chemical evolution of the thermally doped samples were further examined using TGA and FTIR (Figure 44).

Analyzing the TGA results for CA-GLC and all the thermally doped samples, they all tell a similar story of high thermal stability—with all of the samples having weight retention of over 80% even at 800 °C in N₂ atmosphere. CA-GLC had the best response, by retaining about 90% of its initial mass, while TD-GLC₂, TD-GLC₃, and TD-GLC₄ dropped slightly but remained above 80%. Those slightly lower numbers after thiourea treatment are probably related to some of the extra surface groups that were burnt off during the thermogravimetric process [134]. Still, the differences were minor, so thermal doping did not significantly alter the thermal stability of the samples. TD-GLC₃ exhibited intermediate thermal behavior between TD-GLC₂ and TD-GLC₄, suggesting that moderate dopant loading provides additional chemical functionality while maintaining comparatively greater structural stability [177, 178].

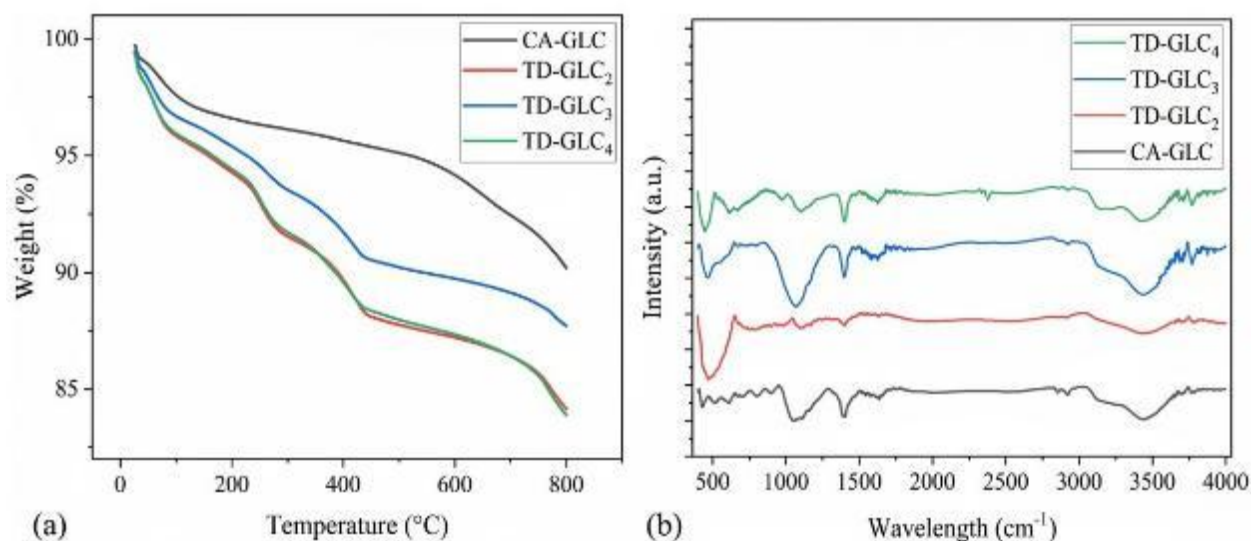


Figure 44. Thermogram (a) and FTIR (b) of the Parent GLC and the thermally doped samples

The FTIR spectra further support the modification of the carbon surface following thermal doping. The CA-GLC spectrum shows characteristic bands associated with oxygen-containing groups and carbon bonding environments [134, 135]. Across the doped samples, several of these bands shift in intensity or definition, indicating gradual changes in surface chemistry rather than abrupt formation of new dominant functionalities. After thiourea treatment, these features change progressively as dopant concentration increases. TD-GLC₂ maintains a spectral profile closely resembling the parent carbon, suggesting minimal structural disruption at lower thiourea concentrations. On the other hand, TD-GLC₃ displays more pronounced features in the C–N/C–O region, highlighting greater integration of heteroatom-containing functional groups. With the highest precursor loading, TD-GLC₄ presents a markedly altered spectral profile. This indicates that excessive thiourea decomposition did not offer further advantage; rather, it resulted in extensive surface reactions and subsequent significant structural changes [179, 180].

The SEM images (Figure 45) indicate progressive morphological changes as thiourea concentration increases, while the corresponding EDX analysis shows the successful incorporation of sulfur into the carbon framework. Sulfur content increases from 1.49 wt% in TD-GLC₂ to 3.76 wt% in TD-GLC₃ and 5.58 wt% in TD-GLC₄, demonstrating the dosage-dependent nature of sulfur introduction. The simultaneous decrease in oxygen content suggests that oxygen-containing groups are removed or replaced during doping. However, since EDX is not reliable for detecting nitrogen, the extent of nitrogen incorporation from thiourea cannot be directly determined by this method [134, 135]. A similar pattern was noted during the hydrothermal doping stage:

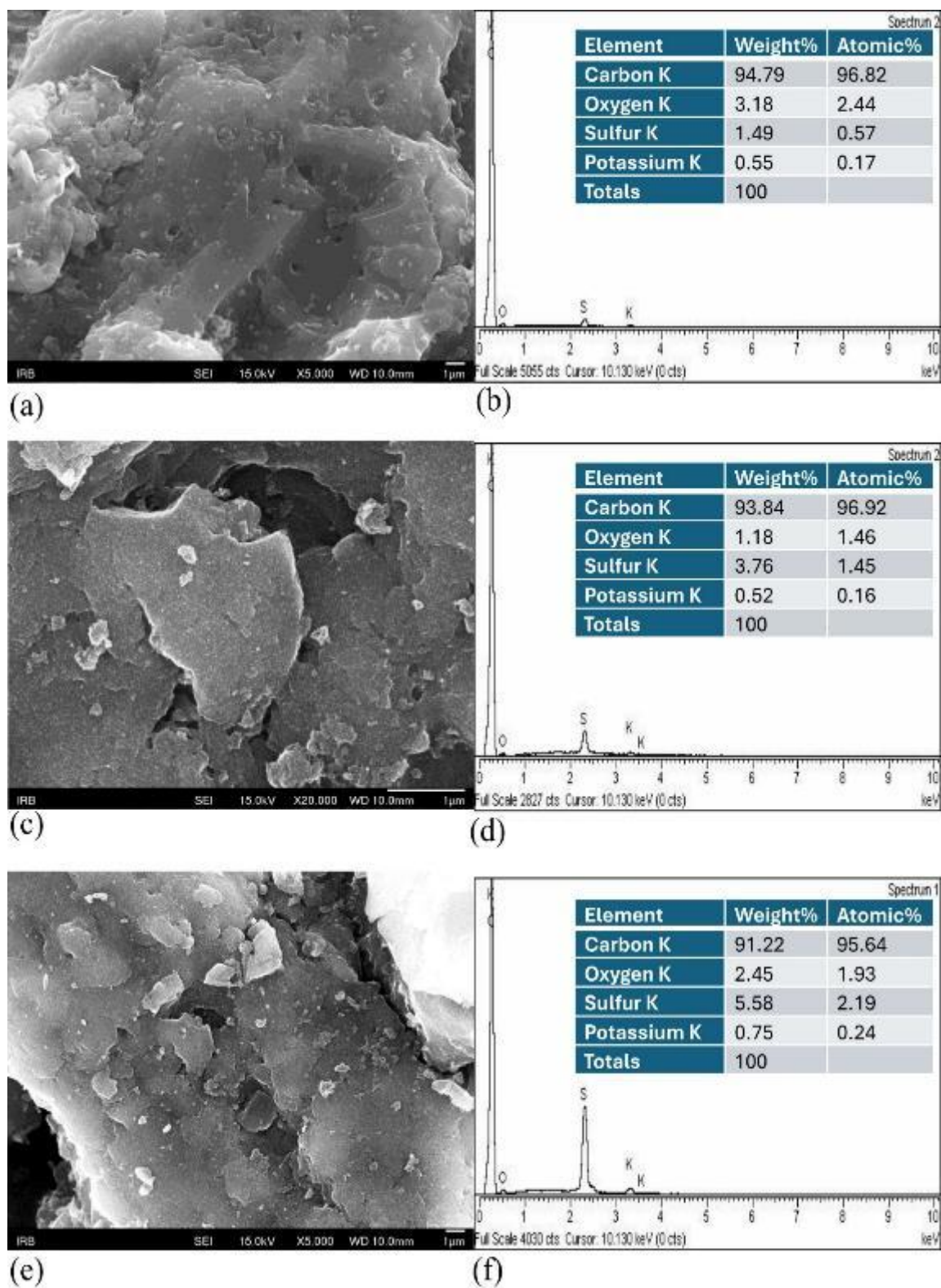


Figure 45. SEM (a,c, and e) and EDX (b, d, and f) of TD-GLC₂, TD-GLC₃, and TD-GLC₄ respectively

EDX confirmed sulfur incorporation, but nitrogen incorporation was only demonstrated through subsequent XPS analysis. Although XPS analysis was not available for the present thermal doping series, the presence of nitrogen-containing functionalities is expected based on the use of thiourea as the dopant precursor and the FTIR features associated with C–N bonding [175, 180]. Further surface chemical analysis would be required for direct confirmation of nitrogen incorporation.

4.4.2.2 Electrochemical Evaluation of Thermally Doped Samples

Electrochemical test results for the thermally doped samples reveal a pattern different from what structural analysis would suggest. As demonstrated by the contrast between the Raman spectra (Figure 46) and the specific capacitance values (Table 33), better graphitic ordering does not always result in better charge storage. Table 33 shows an interesting outcome: TD-GLC₃, despite presenting a more defective carbon structure and a higher ESR (5.88 Ω), achieved the top specific capacitance in GCD testing (109.33 F g⁻¹). Meanwhile, TD-GLC₂, which stood out for structural integrity in both Raman and X-ray diffraction, recorded a much lower GCD capacitance of 50.23 F g⁻¹. This contrast points toward the positive effects of structural defects from higher thiourea loading, possibly due to more surface functional groups and extra active sites that promote electrolyte interaction [7, 54].

Focusing on the cyclic voltammetry (CV) results from Figure 46a, a similar trend appears, but it isn't as pronounced as in the GCD. TD-GLC₂ comes out on top with 87.62 F g⁻¹, followed by TD-GLC₃ at 72.16 F g⁻¹. The difference between CV and GCD values suggests that TD-GLC₃ performs better during slow charge–discharge cycles, maybe due to surface chemistry and ion access playing a bigger role in those conditions [181]. In the case of the TEABF₄/acetonitrile electrolyte, ion movement mostly depends on how easily ions can reach the right spots within the material [6]. Extra nitrogen and sulfur might make the surface more attractive to the electrolyte and open up

new places for ions to stick [56]. However, pushing the modifications too far does not yield positive change. For instance, TD-GLC₄ ended up with the lowest CV capacitance (54.00 F g⁻¹) and the highest ESR (8.94 Ω). Too many defects can get in the way of electronic transport and end up limiting how much charge the material can actually hold [4].

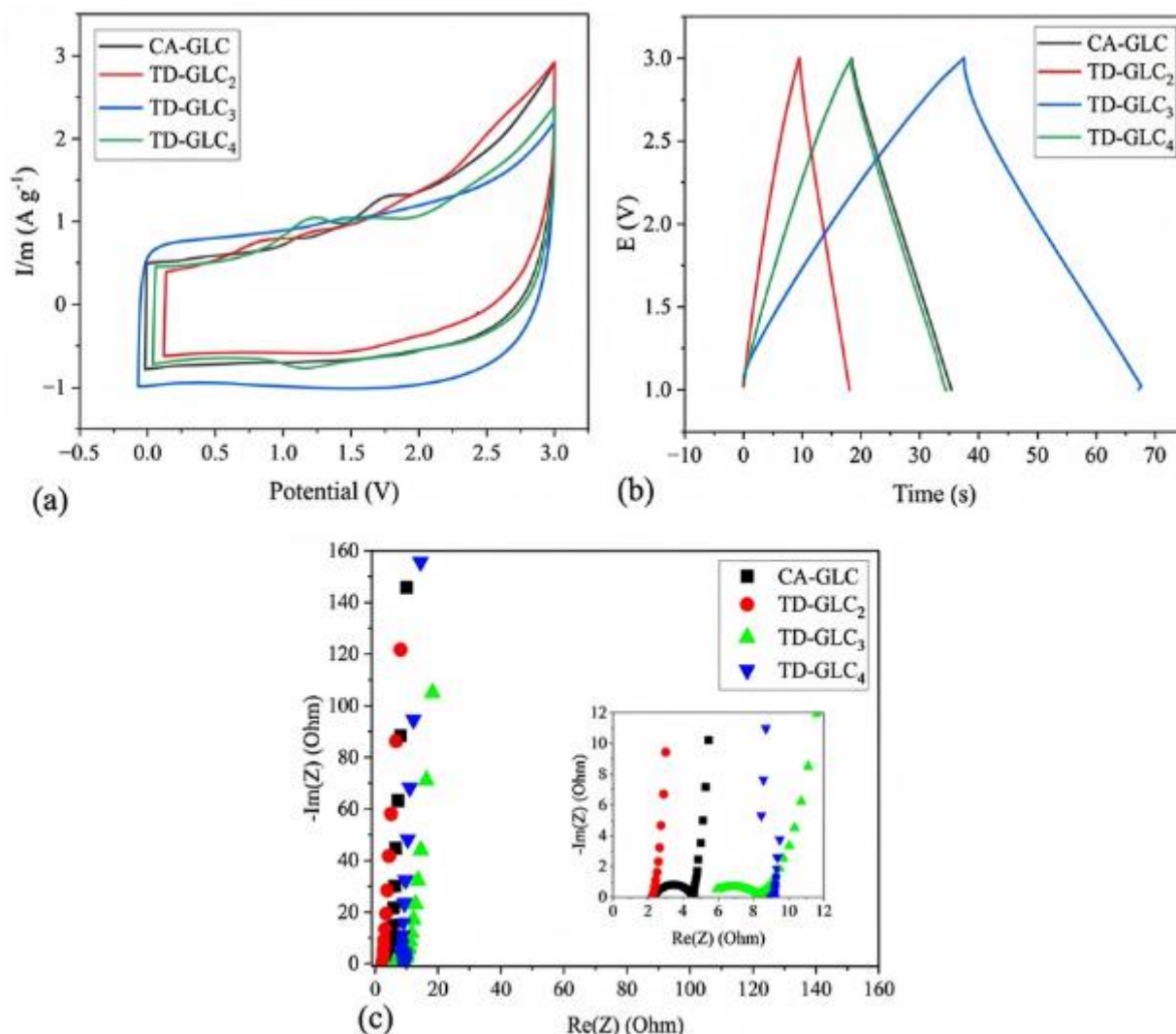


Figure 46. Electrochemical characterization of CA-GLC and thermally doped samples: (a) cyclic voltammetry (CV) curves, (b) galvanostatic charge–discharge (GCD) profiles, and (c) electrochemical impedance spectroscopy (EIS) Nyquist plots.

Looking at ESR values, it becomes clear that a balance between conductivity and surface activity is crucial. TD-GLC₂ had the lowest resistance (2.20 Ω), in line with its orderly graphitic structure,

whereas TD-GLC₃'s higher resistance stemmed from more structural disruption. Yet, the notable GCD capacitance for TD-GLC₃ implies that extra active sites can make up for lower conductivity. All considered, these trends suggest an optimal doping range—enough heteroatoms to boost charge storage, but not so many as to break down the carbon network [55].

To sum up, TD-GLC₂ kept its structural advantages, but TD-GLC₃ managed the best overall electrochemical performance. Higher GCD capacitance supports the idea that a degree of disorder and added functional groups can be beneficial for energy storage [175]. With its rich surface chemistry and defect-heavy structure, TD-GLC₃ was chosen for further nanocomposite work, as these properties should provide more anchoring points for active materials [7].

Table 33. Summary of electrochemical performance metrics for CA-GLC and thermally doped samples.

Sample	CV ($C_s / F\ g^{-1}$)	GCD ($C_s / F\ g^{-1}$)	ESR (Ω)
CA-GLC	63.37	63.10	2.38
TD-GLC ₂	87.62	50.23	2.20
TD-GLC ₃	72.16	109.33	5.88
TD-GLC ₄	54.00	58.07	8.94

4.4.2.3. Selection of Doping Strategy for Downstream Composite Design

In line with the requirement to enhance conductivity, capacitance, and interfacial reactivity through heteroatom doping and surface functionalization [173, 182], both hydrothermal (HD) and thermal doping (TD) routes introduce nitrogen- and sulfur-related functionalities, but with distinctly different structural outcomes. In the current research, the hydrothermal pathway yielded highly active materials, with HD-GLC₇ exhibiting the best overall electrochemical performance because of its balanced conductivity and heteroatom retention. However, this route is relatively time-intensive and tends to produce partially reorganized carbon architecture with lower defect

reachability for subsequent composite integration. In contrast, the thermal doping route generates a more defect-rich and chemically reactive surface, which, despite lower standalone capacitance (as seen for TD-GLC samples), is more advantageous for anchoring secondary phases and enabling further surface functionalization.

Of the three TD samples analyzed, the most favorable compromise was offered by TD-GLC₃, which combined the highest capacitance within the thermal series with a moderate resistance profile while still preserving a sufficiently disordered structure for chemical reactivity. Therefore, although HD materials are superior as standalone electrodes, TD-GLC₃ is selected as the preferred platform for subsequent heteroatom-assisted nanocomposite development due to its faster processing, higher surface defect density, and greater suitability for interfacial modification.

4.4.3. Thermal-Assisted Heteroatom Doping of Sequentially Reduced Graphene Oxide

To investigate the effect of heteroatom incorporation on the selected reduced graphene oxide (CTrGO) and its influence on the structural characteristics of the material, thermal doping was carried out using thiourea as a nitrogen and sulfur precursor. The elevated treatment temperature facilitates the incorporation of heteroatoms into the carbon lattice while simultaneously promoting structural rearrangement within the reduced graphene oxide framework. The same thiourea-to-carbon ratios used previously for the GLC doping study were maintained for the CTrGO samples to allow comparison of the effect of doping across the two carbon systems. The resulting thermally doped materials were designated TD-CTrGO₂, TD-CTrGO₃, and TD-CTrGO₄, corresponding to increasing thiourea-to-CTrGO ratios as described in the methodology. The structural changes induced by thermal doping were subsequently evaluated using Raman spectroscopy and X-ray diffraction analysis.

4.4.3.1. Structural, chemical and morphological evolution during thermal doping

Raman spectra of CTrGO and the thermally doped samples (TD-CTrGO₂, TD-CTrGO₃, and TD-CTrGO₄) exhibited the characteristic D (around 1350 cm⁻¹) and G (close to 1600 cm⁻¹) bands associated with graphene-based carbon materials [40, 61, 62] as shown in Figure 47a. The positions of these bands remained largely unchanged following thermal doping, indicating that the overall graphitic framework was preserved. The I_D/I_G ratios of CTrGO (1.08), TD-CTrGO₂ (1.09), and TD-CTrGO₃ (1.09) were nearly identical, suggesting comparable levels of structural disorder. In contrast, TD-CTrGO₄ displayed a higher I_D/I_G ratio of 1.20, indicating an increase in defect density at the highest thiourea loading. The data generated from the Raman analysis are highlighted in Table 34.

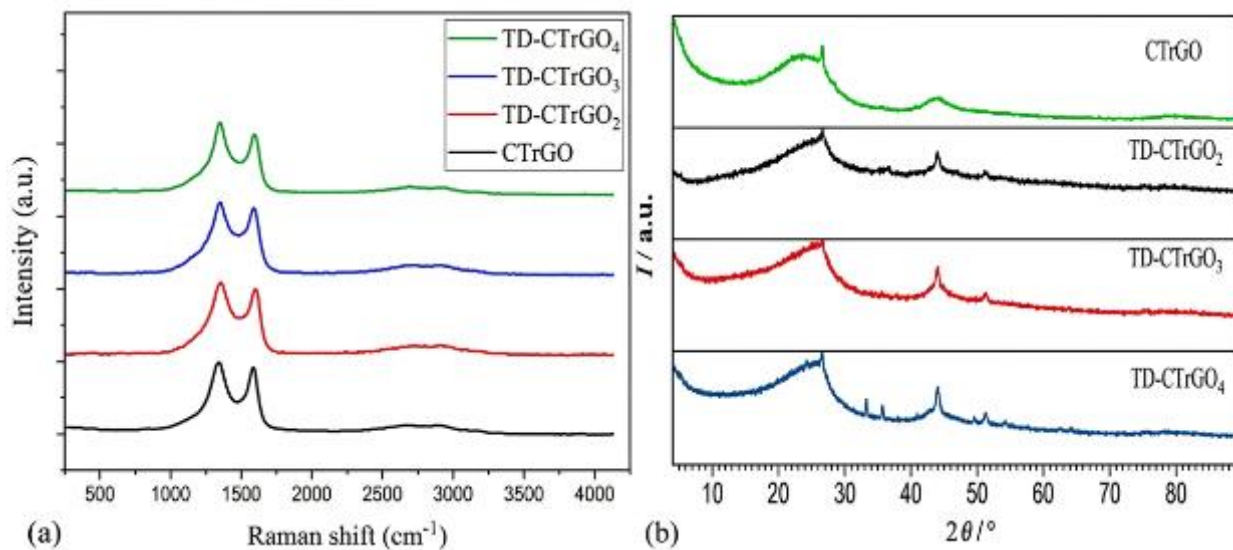


Figure 47. (a) Raman spectra and (b) XRD patterns of CTrGO, TD-CTrGO₂, TD-CTrGO₃, and TD-CTrGO₄ synthesized using increasing thiourea-to-CTrGO ratios through thermal doping.

Furthermore, all samples exhibited broad 2D bands, characteristic of few-layer to multi-layer, highly disordered graphene-like structures rather than well-ordered graphitic layers [183]. All samples showed XRD patterns with a broad diffraction feature centered within the region of 20–

30° 2 θ , which is attributed to (002) reflection of graphitic carbon. This peak is broad due to the turbostratic structure with little long-range ordering, typical of reduced graphene oxide materials [67, 69]. Peak shapes and intensities were slightly different after thermal doping, but no sharp diffraction peaks were added; hence, it is inferred that the thiourea treatment did not give rise to any new crystalline phase.

Table 34. Raman intensity ratios (I_D/I_G and I_{2D}/I_G) for CTrGO and thermally doped reduced graphene oxide samples prepared with increasing thiourea loadings.

Sample	I_D/I_G Ratio	I_{2D}/I_G Ratio
CTrGO	1.08	Broad
TD-CTrGO ₂	1.09	Broad
TD-CTrGO ₃	1.09	Broad
TD-CTrGO ₄	1.20	Broad

The XRD results generally confirmed the Raman results, in that the graphenic carbon framework was not destroyed after doping; only a little change in structure was indicated. Among the doped samples, TD-CTrGO₄ exhibited the greatest degree of disorder, consistent with its higher I_D/I_G ratio.

As seen in Figure 48, SEM combined with EDX analysis was used to examine the surface morphology and elemental composition of the thermally doped rGO samples. The creation of aggregated carbon structures after heat treatment was indicated by the rough and textured carbon surfaces with irregular particle-like characteristics found on all doped samples. The surface of the TD-CTrGO₂ sample was quite rough, with many aggregated particles and noticeable imperfections. TD-CTrGO₃, on the other hand, had a finer surface texture, fewer big protrusions, and a more compact and continuous morphology. Nevertheless, TD-CTrGO₄ had a more heterogeneous surface with repeated particle production and a rougher surface when the thiourea ratio was further increased.

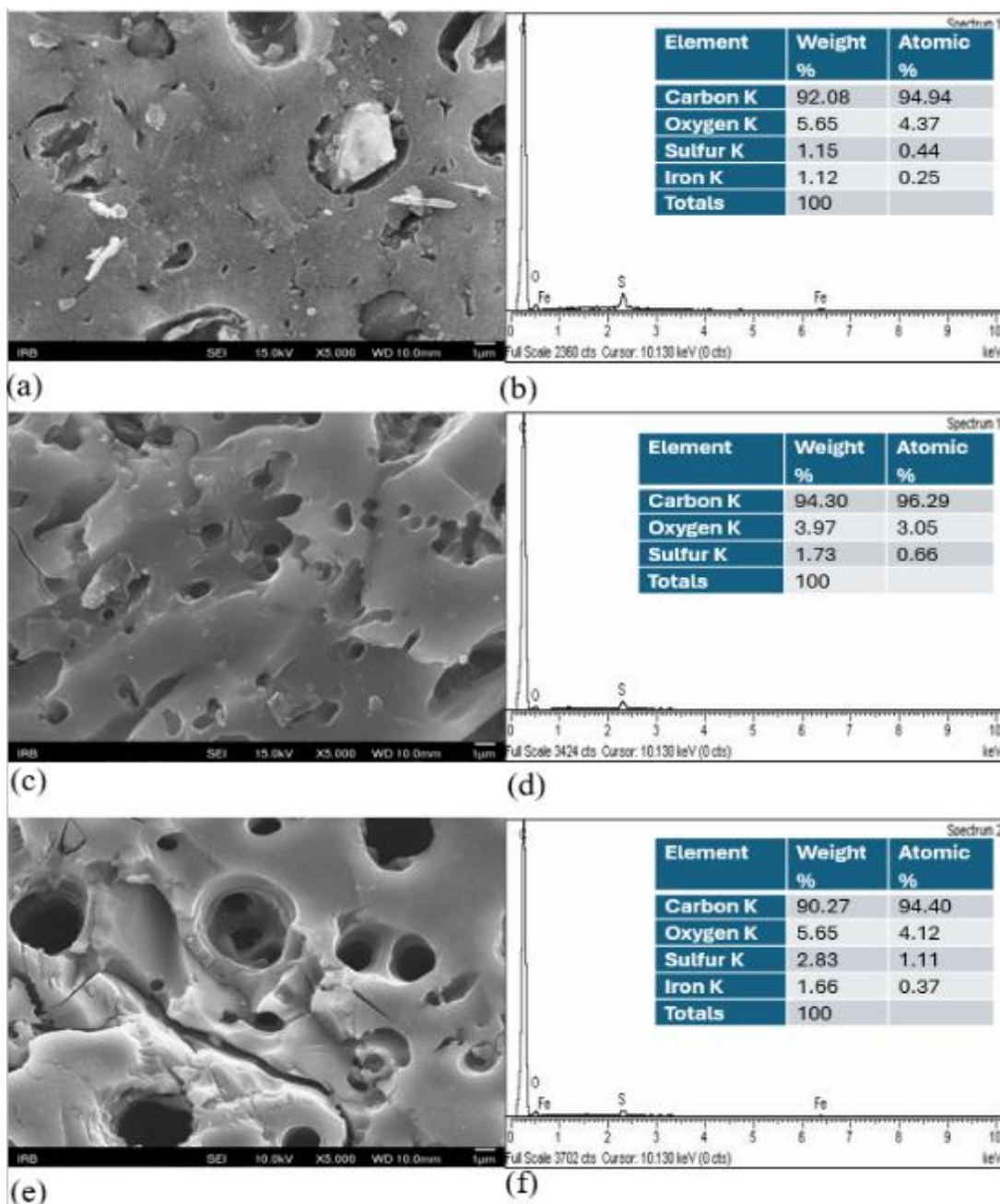


Figure 48. SEM images and corresponding EDX spectra of thermally doped reduced graphene oxide samples: (a,b) TD-CTrGO₂, (c,d) TD-CTrGO₃, and (e,f) TD-CTrGO₄ prepared using increasing thiourea-to-CTrGO ratios.

EDX analysis confirmed that all thermally doped samples were predominantly composed of carbon, with carbon contents ranging from approximately 90–94 wt.%, demonstrating that the carbon framework remained the dominant component after doping. Oxygen was detected in all

samples at relatively low levels, while sulfur was present in each doped material, confirming the incorporation of sulfur-containing species from the thiourea precursor. The sulfur content increased from 0.25 wt.% in CTrGO to TD-CTrGO₂ (1.15 wt.%), TD-CTrGO₃ (1.73 wt.%), and TD-CTrGO₄ (2.83 wt.%), suggesting that higher thiourea loading promoted greater sulfur incorporation. Trace iron was detected in TD-CTrGO₂ and TD-CTrGO₄, whereas it was not observed in the analysed region of TD-CTrGO₃, which may be attributed to local variation within the sample. As stated earlier in the analyses of thermally doped graphene-like carbons (TD-GLC₂ to TD-GLC₄), nitrogen could not be detected by EDX, but considering that sulfur content increased after doping, suggests that nitrogen was likely incorporated into CTrGO as well. Overall, the SEM and EDX results indicate that thermal doping preserved the carbon-rich framework while introducing sulfur heteroatoms and modifying the surface morphology depending on the thiourea ratio.

4.4.3.2. Electrochemical Evaluation of Thermally Doped rGO Samples

The electrochemical performance of CTrGO and the thermally doped samples demonstrates that structural modification alone does not directly translate into improved charge storage behaviour [54, 55, 58]. Figure 49 illustrates the electrochemical properties of the doped rGO against the parent rGO and Table 35 summarizes the capacitance values obtained from cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and the corresponding equivalent series resistance (ESR). Unlike the thermally doped GLC samples, where an intermediate doping level produced the highest capacitance, the rGO-based samples showed a more gradual improvement, with TD-CTrGO₄ exhibiting the best overall electrochemical response amongst the three samples tested.

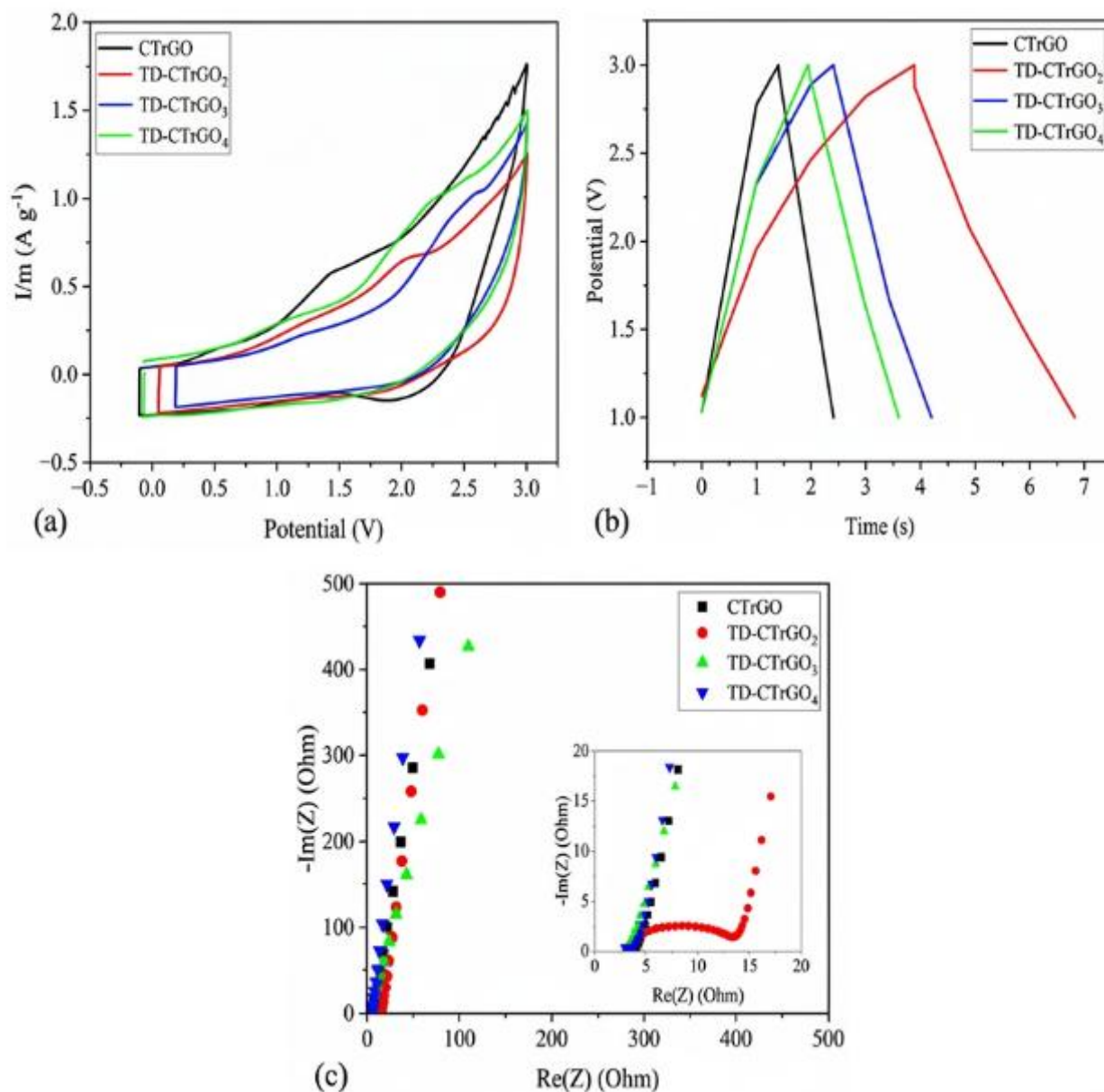


Figure 49. Electrochemical characterization of CTrGO as the starting material, and the thermally doped samples: (a) cyclic voltammetry (CV) curves, (b) galvanostatic charge–discharge (GCD) profiles, and (c) electrochemical impedance spectroscopy (EIS) Nyquist plots.

CTrGO serving as the baseline for the electrochemical analysis showed a comparatively low GCD capacitance of 4.74 F g⁻¹ and a CV capacitance of 29.20 F g⁻¹. TD-CTrGO₂ and TD-CTrGO₃ displayed somewhat lower CV values (13.16 and 12.40 F g⁻¹, respectively, based on cyclic voltammetry method) after thermal doping, indicating that decreased thiourea loading did not

sufficiently increase surface activity to offset potential changes in conductivity and surface structure. TD-CTrGO₄, on the other hand, obtained the largest capacitance values—33.49 F g⁻¹ from CV and 16.84 F g⁻¹ from GCD. This improvement agrees with the observations made from Raman and EDX analyses, where TD-CTrGO₄ exhibited the highest defect density and sulfur content among the samples investigated. These structural features may contribute to enhanced electrolyte interaction by introducing additional defect-associated sites [79, 173, 181]; however, the exact contribution of surface functional groups would require further chemical characterization.

Table 35. Electrochemical performance parameters of CTrGO and thermally doped rGO samples.

Sample	CV ($C_s / F g^{-1}$)	GCD ($C_s / F g^{-1}$)	ESR (Ω)
CTrGO	29.20	4.74	3.37
TD-CTrGO ₂	13.16	4.52	3.71
TD-CTrGO ₃	12.40	5.59	2.95
TD-CTrGO ₄	33.49	16.84	2.94

The overall capacitance values are relatively low. This behavior might have more to do with the testing environment than just the materials' inherent qualities. Highly faulty carbon structures may undergo greater electrochemical stress under such harsh conditions, which would restrict ion accessibility and decrease the effective contribution of surface functional groups [6, 53]. Furthermore, charge transport channels might be adversely affected by excessive structural disorder, which lessens the advantage of having more heteroatom sites [77, 167, 181].

The ESR values followed a similar trend, with TD-CTrGO₄ showing the lowest resistance among the doped samples (2.94 Ω), closely followed by TD-CTrGO₃ (2.95 Ω). This suggests that although TD-CTrGO₄ possessed a more defective structure, the thermal treatment maintained sufficient conductivity within the carbon framework. Overall, the results indicate that higher thiourea loading

was favourable for the rGO system, with TD-CTrGO₄ providing the best balance between defect generation, heteroatom incorporation, and electrical transport. However, further electrochemical optimization would likely be required to fully exploit the potential of these thermally doped rGO materials. But for this research, TD-CTrGO₄ will be used for the making of the nanocomposite under the conditions TD-GLC₃ was used in the making of the nanocomposite in that route.

4.5. TGFS Nanocomposite Development on Thermally Doped Carbon

Building upon the identification of TD-GLC₃ as the optimal support material, iron oxide–silica nanocomposites were integrated into it to rigorously assess the capacity of the defect-rich, heteroatom-doped carbon framework to serve as a versatile scaffold for the addition of secondary phases. This approach was predicated on the hypothesis that the formation of TGFS composites would not only introduce additional electrochemically active sites but also maintain the requisite graphitic connectivity for efficient charge transport. In deliberately adjusting the proportions of iron oxide and silica precursors, the intention was to observe firsthand how subtle compositional shifts might reshape the structural organization, guide the emergence of new phases, and influence the intricate interactions between the carbon host and its inorganic guests. Through this hands-on, comparative approach, it is hoped to move beyond surface-level characterization and instead illuminate the deeper relationship between the structural design of the materials and their resulting electrochemical behavior. Additionally, this section includes the nanocomposite made with TD-CTrGO₄, which is based on the best-performing TGFS nanocomposite, with the goal of observing how it fared structurally in comparison to the parent material and the TGFS made with the same precursor composition.

4.5.1. Structural, chemical, and morphological evolution of TGFS Nanocomposites

Structural evolution of TGFS nanocomposites was measured against the thermally doped carbon support (TD-GLC₃), the baseline before making the nanocomposite.

Based on the Raman spectra (Figure 50), TD-GLC₃ showed a highly defective carbon framework, with a high Raman defect ratio ($I_D/I_G = 1.03$) and an indistinct 2D band, indicating structural disruption from the thiourea doping process [80, 174, 181]. After in situ oxidative formation of iron oxide–SiO₂ phases at 350 °C, structural modification varied significantly with precursor composition [89, 91, 97, 98, 100].

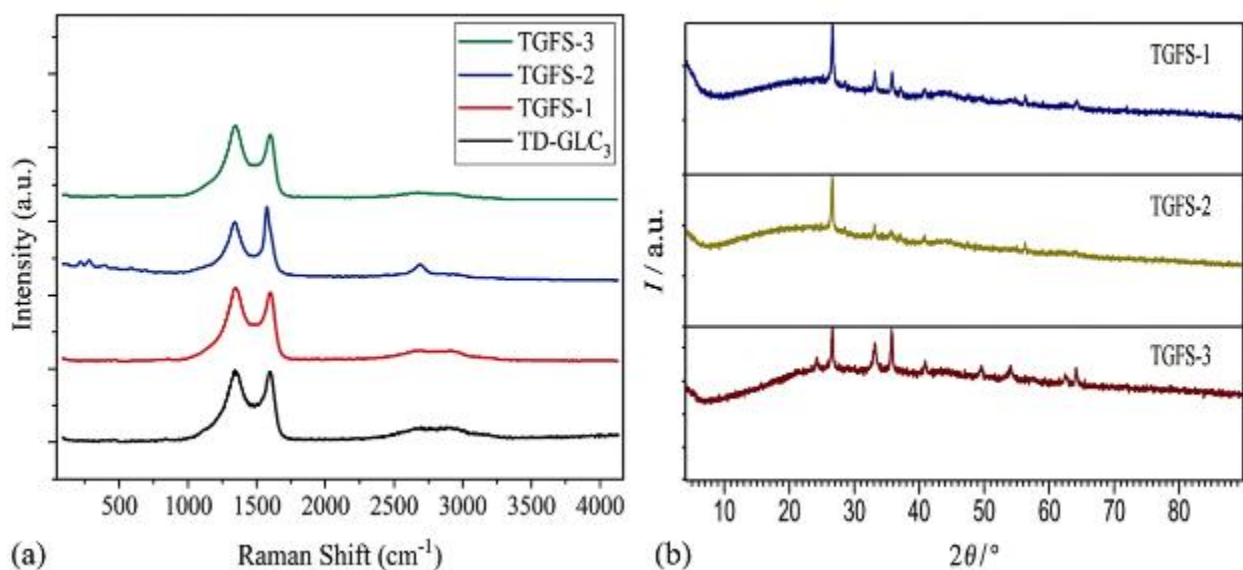


Figure 50. Raman of TD-GLC₃ and the resulting nanocomposites (a) and the XRD patterns (b) of the nanocomposites

Among the compositions investigated, TGFS-2 (80:15:5) exhibited the most favorable structural evolution. The defect ratio decreased from 1.03 to 0.79, and a distinguishable 2D band ($I_{2D}/I_G = 0.22$) emerged. This indicates that some restoration of ordered sp² domains occurred. However, this defect ratio remains very high, reflecting only a partial improvement. XRD analysis (Figure 46b) is in close agreement with the Raman assessment, as TGFS-2 retained a graphitic (002)

reflection near 26.5° and sharp reflections for crystalline iron oxide phases [89, 95, 96]. The oxidative calcination process most likely eliminated some highly disordered carbon, but this didn't address the majority of the persisting disorder that remained even after treatment.

Table 36. Raman-derived structural parameters of TD-GLC₃ and TGFS nanocomposites.

Sample	I_D/I_G Ratio	I_{2D}/I_G Ratio
TD-GLC ₃	1.03	Broad
TGFS-1	1.08	Broad
TGFS-2	0.79	0.22
TGFS-3	1.14	Broad

In contrast, TGFS-1 and TGFS-3 exhibited less favourable structural changes. TGFS-1, prepared with the highest iron precursor content, showed an increased defect ratio ($I_D/I_G = 1.08$) and reduced definition of the graphitic reflections, suggesting excessive oxidative interaction between the forming iron oxide phase and the carbon framework [90, 91]. This indicates that while iron oxide formation can promote structural modification at appropriate concentrations, excessive loading may accelerate carbon degradation [95, 100]. Similarly, TGFS-3 displayed the highest defect ratio ($I_D/I_G = 1.14$) and weakened graphitic features. The higher silica contribution and reduced iron oxide content likely altered phase development, limiting effective interaction between the carbon support and iron oxide species during calcination [97, 98].

The thermal stability and surface chemical characteristics of the TGFS nanocomposites were further examined using TGA and FTIR analysis (Figure 51). The TGA profiles of TD-GLC₃, TGFS-1, TGFS-2, and TGFS-3 exhibited similar gradual, multi-step weight loss behavior from room temperature to approximately 900 °C. Looking at the thermograms, the three nanocomposites recorded initial low-temperature mass loss followed by a slower decrease at higher temperatures. However, the curves remained considerably separated throughout the heating

range, indicating differences in thermal response among the samples. At 800 °C, TD-GLC₃ and TGFS-1 showed comparable residual masses of 87.70% and 87.82%, respectively, while TGFS-2 and TGFS-3 retained lower masses of 83.93% and 79.71%. The progressive reduction in residual mass from TGFS-1 to TGFS-3 indicates that the different composite compositions influence the thermal decomposition behavior of the carbon-based framework.

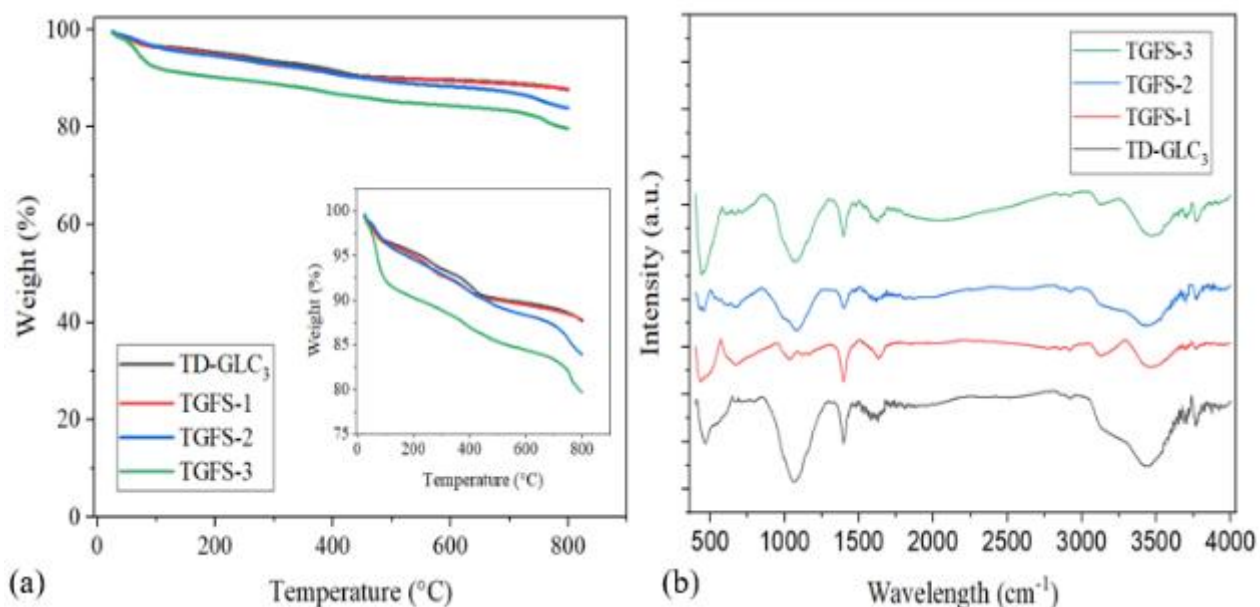


Figure 51. TGA (a) and FTIR (b) characterization of TD-GLC₃ and TGFS nanocomposites.

All samples displayed FTIR spectra that were relatively similar in their band positions, with the main bands appearing at nearly the same positions across the measured range. They all had a broad band in the 3000–3600 cm⁻¹ region, a noticeable band around 1600 cm⁻¹, and some additional features between 1000 and 1200 cm⁻¹. While there were small differences in the intensity of these bands, the fact that the peak positions remained mostly the same suggests that the making of the composites did not have a significant impact on the types of chemical bonds on the surface. This could be related to the use of small quantities of ferric oxide and silicon (II) oxide sources. Instead, the observed variations indicate changes in the relative contribution of existing functional groups following incorporation of the inorganic phases [97-99].

In addition to other analyses, the SEM images for the nanocomposites revealed that the nanocomposite morphology changed with precursor composition. TGFS-1 (Figure 52a) exhibited a rough, highly aggregated surface made of irregular particles and layered carbon fragments, suggesting extensive deposition of inorganic phases on the carbon support. TGFS-2 presents clusters of angular, block-shaped particles interspersed with distinct voids, reflecting a more fragmented distribution of the deposited phases. In contrast, TGFS-3 maintains a coherent sheet-like architecture, where stacked graphene-like layers remain evident despite the incorporation of inorganic components. The preservation of these layered features suggests that the carbon framework experienced less surface coverage than in TGFS-1.

Though the earlier FTIR did not show new peaks in the nanocomposites in comparison to the TD-GLC3, the EDX results as shown in Table 37 confirm successful incorporation of the inorganic phases into all three nanocomposites. Carbon remained the dominant element, accounting for approximately 58–71 wt.%, indicating that the graphene-like framework was preserved after composite formation. Among the three samples, TGFS-1 showed the highest iron content at 26.47 wt.%, while TGFS-2 had the lowest at 10.12 wt.%, followed by an increase to 14.67 wt.% in TGFS-3. Silicon was detected in all three samples, with its content increasing from 0.82 wt.% in TGFS-1 to 2.64 and 2.79 wt.% in TGFS-2 and TGFS-3, respectively. Sulfur was also detected in each sample, although its content varied between 0.85 and 2.00 wt.%. As expected, differences in iron and silicon contents reflected the ratios of the precursor used during synthesis. Oxygen was detected in all samples. This reflects the presence of iron oxide, silica, and residual oxygen-containing groups on the carbon surface. Although most of the oxygen content is due to the oxides, the EDX of TD-GLC3 shows the extent to which oxygen content increased in TGFS 1-3.

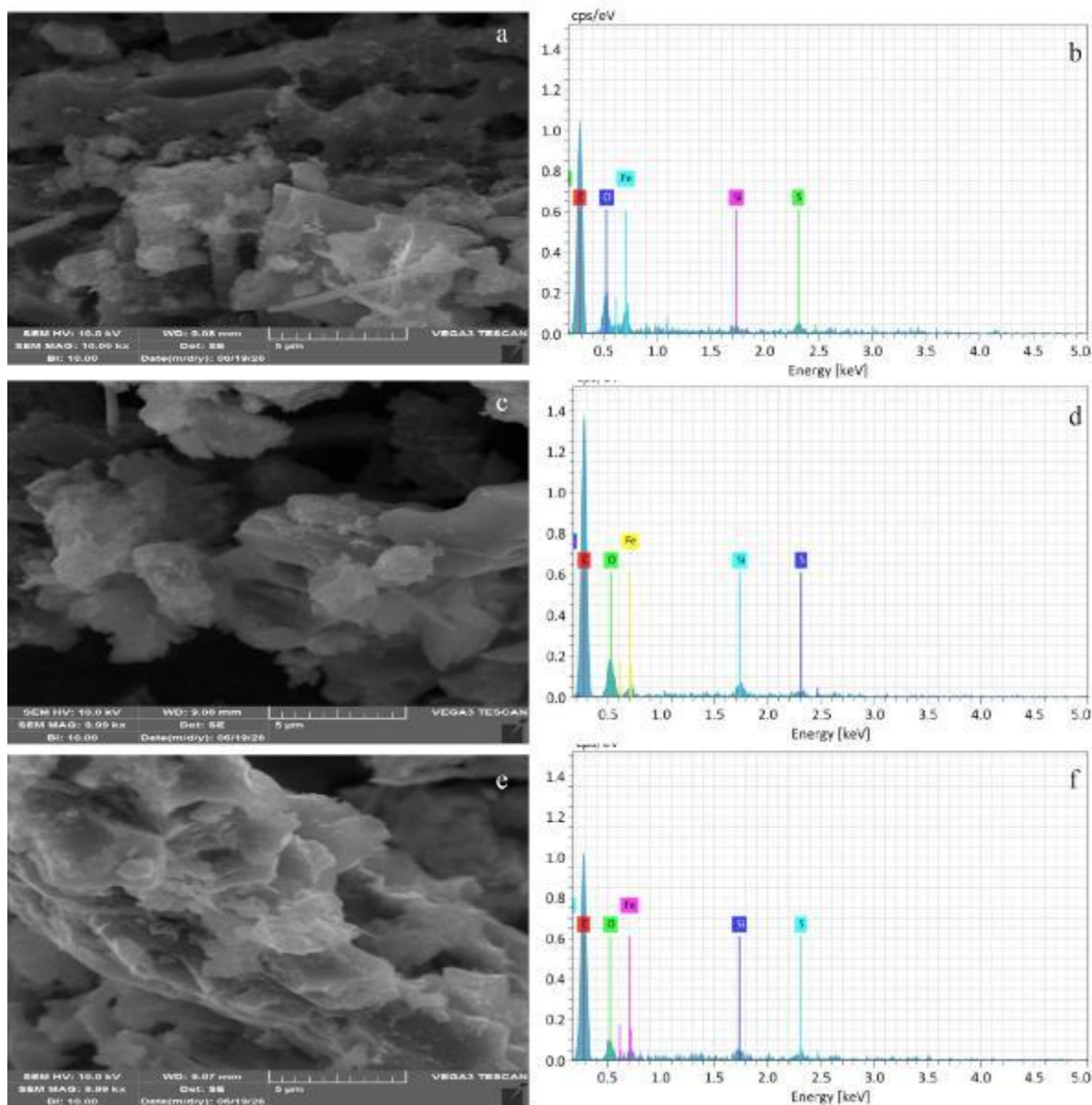


Figure 52. SEM micrographs (a, c, e) and corresponding EDX analysis (b, d, f) of TGFS-1, TGFS-2, and TGFS-3 nanocomposites.

This suggests that the lower the oxide content of the nanocomposites, the greater the retention of the dopants. In addition, it indicates that the dopants such as sulfur introduced during thiourea doping remained at least partially preserved throughout the composite fabrication process, although its distribution varied among the different formulations.

Table 37. Elemental composition (wt.% and at.%) of TGFS nanocomposites determined by EDX analysis.

Element	TGFS-1		TGFS-2		TGFS-3	
	Wt%	At%	Wt%	At%	Wt%	At%
Carbon	58.02	77.89	70.52	81.95	70.69	84.98
Oxygen	13.09	13.20	15.87	13.84	9.85	8.89
Iron	26.47	7.64	10.12	2.53	14.67	3.79
Silicon	0.82	0.47	2.64	1.31	2.79	1.44
Sulfur	1.60	0.81	0.85	0.37	2.00	0.90
Totals	100	100	100	100	100	100

Together, the SEM and EDX results demonstrate that altering the precursor composition influenced both morphology and elemental distribution while maintaining the overall carbon-based framework.

4.5.2. Electrochemical Performance of TGFS Nanocomposites

The electrochemical performance of the TGFS nanocomposites is interpreted within the context of the organic electrolyte system (TEABF₄/acetonitrile), where charge-storage behaviour differs from that commonly observed in aqueous electrolytes [5, 6, 54, 58]. In organic electrolytes, the larger electrolyte ions, weaker surface redox contribution, and slower ion diffusion kinetics mean that improvements associated with heteroatom functionality or metal oxide phases may not translate directly into higher capacitance [5, 6, 58].

The electrochemical behaviour of TD-GLC3 and the TGFS nanocomposites is shown in Figure 53. The cyclic voltammograms in Figure 53a display clear capacitive profiles for all samples, with TD-GLC3 enclosing the largest area. Among the composites, TGFS-3 shows the broadest CV response, followed by TGFS-1, while TGFS-2 exhibits the smallest area. These differences reflect how the incorporation of iron oxide–silica phases affect the accessible surface and ion-interaction sites in the organic electrolyte. As shown in Table 38, the incorporation of iron oxide–silica phases

resulted in lower capacitance values compared with the TD-GLC₃ support, suggesting that the introduced inorganic phases modified the carbon/electrolyte interface rather than simply increasing charge-storage capability [89-91, 97, 98].

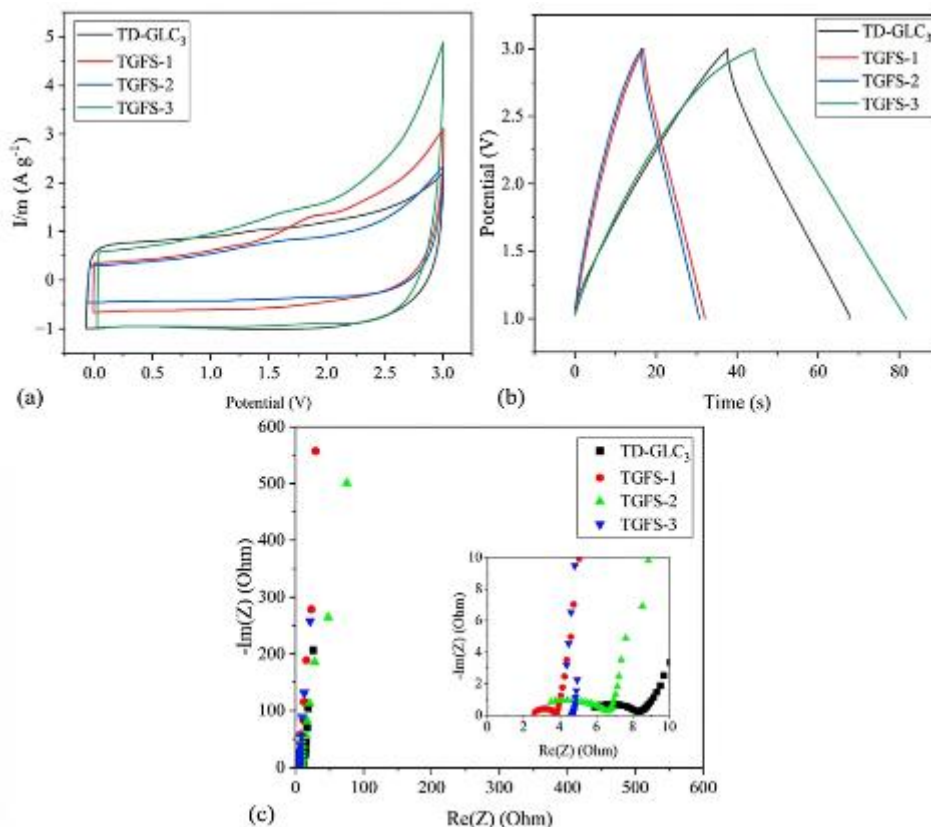


Figure 53: Electrochemical characterization of TD-GLC₃ and TGFS nanocomposites: (a) cyclic voltammetry, (b) galvanostatic charge–discharge, and (c) Nyquist plots.

Based on GCD extracted data from Figure 53b, TGFS-3 performed best for capacitance ($59.33\ F\ g^{-1}$), with TGFS-1 next ($51.73\ F\ g^{-1}$) and TGFS-2 trailing ($30.29\ F\ g^{-1}$). This result goes against the patterns observed in structural tests. TGFS-2 looked the most structurally ordered but ended up with the lowest capacitance. In this system, better ordering does not always help. A more ordered structure can mean fewer places for the electrolyte to reach, which can hold back performance even when conductivity improves [53, 54, 148].

TGFS-3, even with more defects, surprisingly performed better in some ways when the electrochemical data is analyzed. This might be due to the presence of more defects that could have led to the opening of extra spots for the electrolyte to interact, which helps with charge storage [90, 100]. But there's a tradeoff based on the Nyquist plot's (Figure 53c) derived equivalent series resistance, where TGFS-3 also had a higher ESR (4.59 Ω), which might be because the same defects affected the ion transport kinetics in this sample [54]. The results show it is all about finding the right middle ground: enough conductivity for charge flow, the right amount of defects for active sites, and good access for the ions. Crystallinity, or the amount of the inorganic material that is available, is not the only factor that matters in this instance [87].

Table 38. Specific capacitance and equivalent series resistance of TD-GLC₃ and TGFS nanocomposites in TEABF₄/acetonitrile electrolyte.

Sample	CV ($C_s / F g^{-1}$)	GCD ($C_s / F g^{-1}$)	ESR (Ω)
TD-GLC ₃	72.16	109.33	5.88
TGFS-1	51.40	51.73	2.58
TGFS-2	23.96	30.29	3.50
TGFS-3	36.28	59.33	4.59

TD-GLC₃ is shown for reference because it served as the carbon base for nanocomposite formation, as such its electrochemical data is serving the purpose baseline metrics. The defect-rich surface generated during thermal doping provides favorable anchoring sites for inorganic phases while preserving sufficient graphitic connectivity for electron transport [80]. These characteristics make TD-GLC₃ a suitable scaffold for evaluating the influence of iron oxide–silica incorporation on structural and electrochemical behavior.

Considering both structural and electrochemical performance, TGFS-1 provides the most favorable overall balance among the investigated nanocomposites. While TGFS-2 exhibited the greatest degree of structural restoration, its capacitance was significantly lower than those of

TGFS-1 and TGFS-3. Conversely, TGFS-3 achieved the highest capacitance but at the expense of increased resistance and greater structural disorder. TGFS-1 combined relatively good structural integrity with the lowest equivalent series resistance and competitive capacitance, indicating a more effective balance between conductivity, accessible active sites, and carbon framework preservation.

These findings demonstrate that precursor ratio strongly influences the interaction between the carbon support and the inorganic phases [97, 98]. The composition represented by TGFS-1 therefore offers the most suitable design strategy for subsequent nanocomposite development. Accordingly, the precursor proportions and processing conditions identified in TGFS-1 were selected as the basis for extending the nanocomposite approach to reduced graphene oxide (rGO)-based systems, where the higher conductivity of the rGO framework is expected to further enhance interfacial charge transport and electrochemical performance [87, 102].

4.5.3 Structural, chemical, and morphological evolution of the TCGFS nanocomposite

The structural evolution of TCGFS was evaluated relative to its parent carbon (TD-C_{Tr}GO₄) and compared with TGFS-1, which was synthesized using the same precursor quantities. Based on the Raman spectroscopic analysis (Figure 54a), TD-C_{Tr}GO₄ exhibited a highly defective carbon framework with an I_D/I_G ratio of 1.20, indicating significant structural disorder introduced during thiourea-assisted thermal doping. After composite formation, the I_D/I_G ratio of TCGFS decreased to 1.03, suggesting partial defect relaxation and rearrangement of the carbon structure during calcination. This structural modification was also reflected in the XRD pattern as shown in Figure 54b, where TCGFS exhibited a more defined (002) reflection compared to what was observed

earlier in the parent carbon (TD-CTrGO₄) in Figure 47b. However, the peak position at approximately 24.14° indicates an expanded interlayer spacing relative to crystalline graphite, confirming that the carbon framework remained turbostratic rather than highly ordered [13, 140].

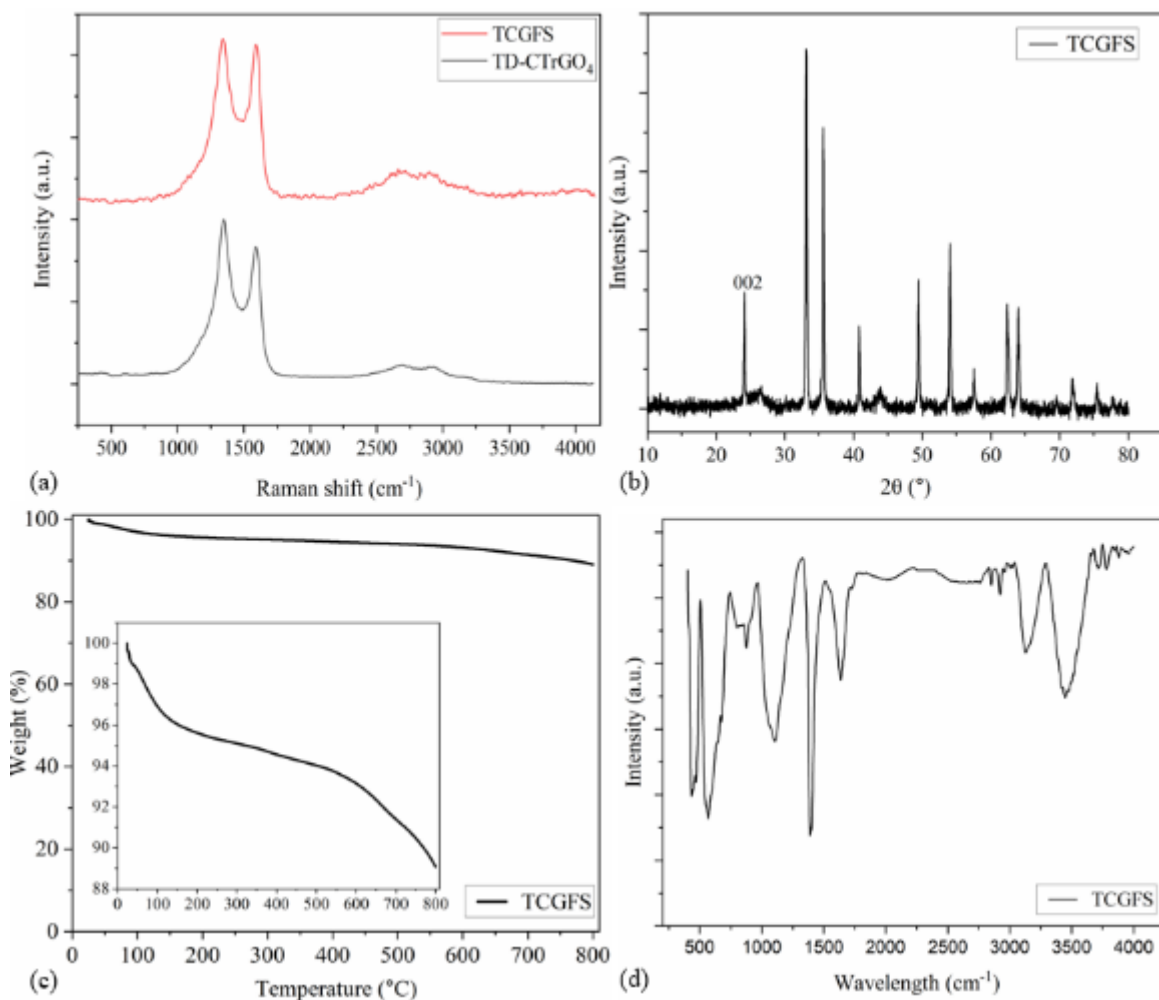


Figure 54. Structural and chemical characterization of TCGFS using Raman (a), XRD (b), TGA (c), and FTIR (d) analyses.

The structural characteristics of TCGFS differed from those of TGFS-1 despite the identical precursor loading. TGFS-1 exhibited a (002) reflection closer to 26.5°, indicating a more compact stacking arrangement of the graphenic layers, whereas the lower-angle shift observed for TCGFS suggests greater interlayer expansion and a less ordered stacking configuration [13, 89]. This difference can be attributed to the distinct nature of the starting carbon materials. The GLC-derived

carbon used in TGFS-1 possessed a more organized framework before the formation of the nanocomposite, while TD-CTrGO₄ contained a higher concentration of structural defects, which influenced the final carbon arrangement after incorporation of the Fe₂O₃/Fe₃O₄–SiO₂ phases. Nevertheless, the decrease in I_D/I_G and the sharpening of the (002) reflection indicate that TCGFS underwent partial structural reorganization during composite formation.

The thermal behaviour of TCGFS (Figure 54c) showed the gradual multi-step decomposition profile characteristic of the composite materials. Although TGA data for TD-CTrGO₄ were not obtained, the similarity between the thermal response of TCGFS and TGFS-1 (Figure 51a), with both samples having around 87 to 88% retention, suggests that the Fe₂O₃/Fe₃O₄–SiO₂ phases and overall composite composition largely determine the degradation behaviour. FTIR analysis shown in Figure 54d further confirmed successful incorporation of the inorganic phases, with TCGFS displaying characteristic bands associated with O–H stretching, C=C skeletal vibrations, Si–O, and Fe–O bonding [95-98]. The absence of additional absorption features suggests that composite formation modified the existing carbon–oxide interactions rather than generating new surface functional groups.

SEM analysis (Figure 55a) revealed a rough and heterogeneous morphology, likely consisting of irregular oxide deposition across the carbon surface. Compared with TGFS-1, TCGFS exhibited a more aggregated appearance, which may be related to the highly defective nature of TD-CTrGO₄. The larger number of structural imperfections in the rGO-derived carbon may provide additional nucleation sites for oxide formation, resulting in less uniform particle distribution [89, 96]. From Figure 55b, the EDX analysis confirmed the successful incorporation of Fe and Si into the composite, with measured contents of 31.25 wt.% Fe and 0.98 wt.% Si (Table 39). The carbon content of TCGFS was 51.92 wt.%, indicating a significant contribution from the inorganic phases.

The sulfur content of 0.53 wt.% suggests partial loss of sulfur-containing species during calcination, consistent with the thermal treatment of the thiourea-doped carbon framework.

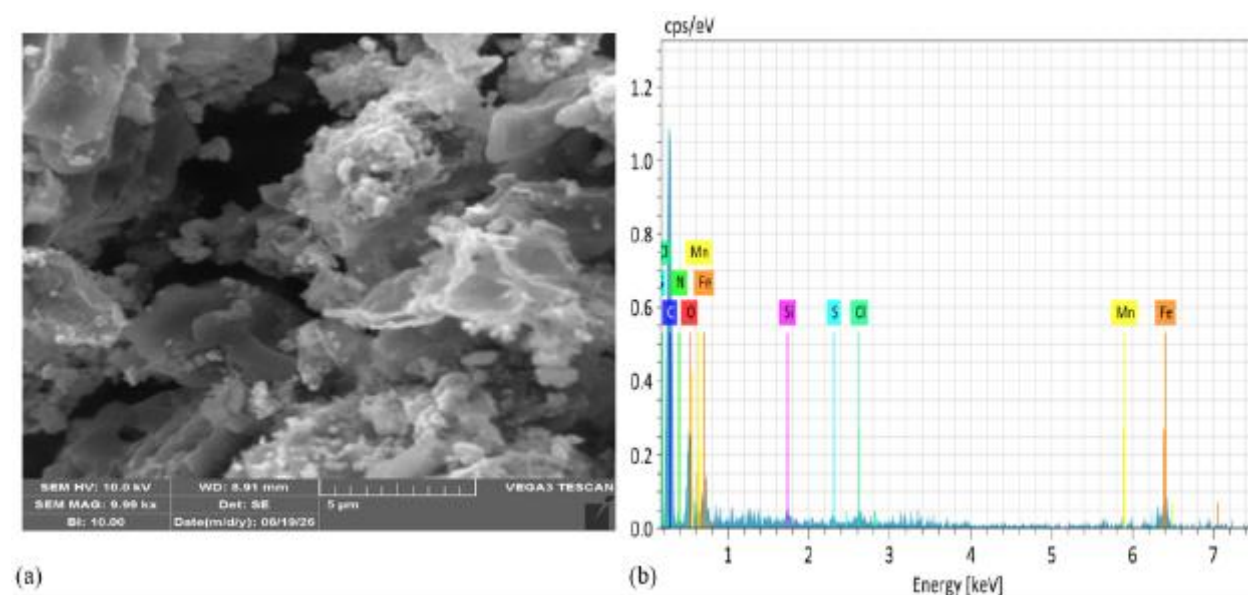


Figure 55. (a) SEM micrograph of TCGFS and (b) EDS spectrum showing its elemental composition.

Overall, the comparison between TCGFS and TGFS-1 demonstrates that the carbon precursor strongly influences the structural and morphological evolution of the composite, even when identical precursor quantities are used. While TCGFS experienced partial structural reorganization after incorporation of the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4\text{-SiO}_2$ phases, the expanded interlayer spacing and greater aggregation reflect the influence of the initially defective TD-C TrGO_4 framework.

Table 39. Elemental composition of TCGFS obtained from EDS (weight% and atomic%)

Element	Weight%	Atomic%
Carbon K	51.92	73.69
Oxygen K	14.49	15.44
Iron K	31.25	9.54
Silicon K	0.98	0.60
Chlorine K	0.75	0.36
Sulphur K	0.53	0.28
Nitrogen K	0.08	0.10
Manganese K	0.00	0.00
Total	100	100

These results highlight the importance of the carbon support in controlling defect evolution, layer organization, and inorganic phase distribution within the final nanocomposite.

4.5.4. Electrochemical Performance of TCGFS Nanocomposite

To see how the introduction of $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4\text{-SiO}_2$ affects charge storage, TCGFS's performance was compared to that of TD-C TrGO_4 , the parent carbon material from which it was made, and TGFS-1, the nanocomposite from the other studied pathway that was made using the same ratio of Fe, Si, and carbon precursors. TEABF $_4$ /acetonitrile electrolyte was used as before, which made it possible to focus mostly on ion movement, carbon framework conductivity, and surface interactions, and not the strong pseudocapacitance that is commonly observed in water-based systems. Specifically, metal oxides can alter the electrode/electrolyte interphase by providing more electrochemically active sites in a way sensitive to electrolyte environment, oxide size, and dispersion, and carbon matrix interaction [90, 95, 96]. The CV, GCD, and EIS of the synthesized nanocomposite can be seen in Figure 56.

Based on Table 40, TD-C TrGO_4 recorded a CV capacitance of 33.49 F g $^{-1}$ and a GCD capacitance of 16.84 F g $^{-1}$, with ESR at 2.94 Ω . Once we introduced $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4\text{-SiO}_2$, TCGFS dropped slightly to 28.30 F g $^{-1}$ (CV) but jumped to 25.00 F g $^{-1}$ (GCD). That is an indication that composite formation in this study does not just boost total charge storage, rather it also modifies how the electrode behaves, especially at the carbon–oxide boundary and during charge transfer. Although composites of iron oxide/carbon with improved charge-storage behaviour are reported frequently, the improvements are usually observed for aqueous electrolytes where tentatively redox activity associated with iron oxide dominates capacitance contribution [89, 96, 100]. In this current organic

electrolyte system, the effects of oxide incorporation are thus much more relevant to modifications in interfacial structure, conductivity and ion accessibility.

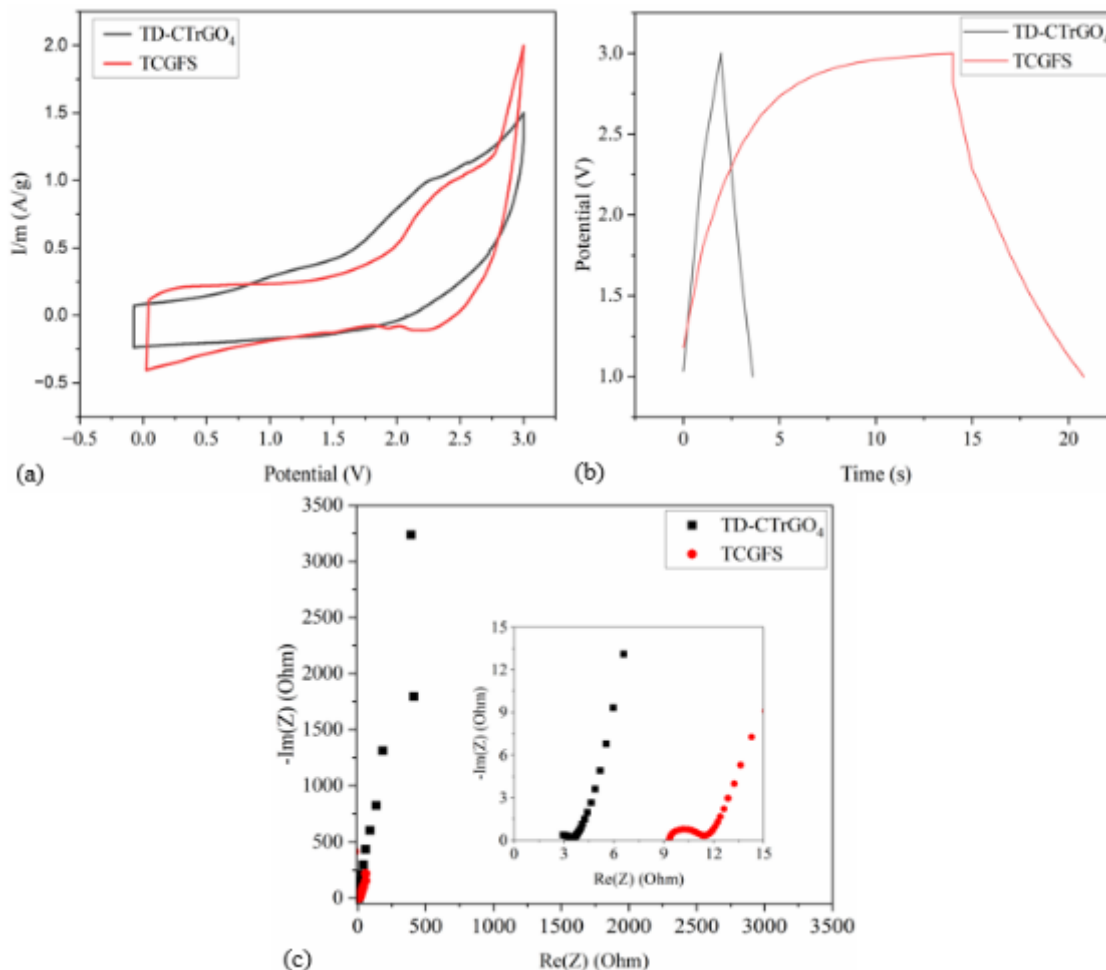


Figure 56. Electrochemical characterization of TD-CrGO₄ and TCGFS: (a) cyclic voltammetry, (b) galvanostatic charge–discharge, and (c) Nyquist plots.

Furthermore, the improved specific capacitance of TCGFS's recorded during GCD analysis came at the cost of higher resistance. ESR nearly tripled, from 2.94 Ω to 9.32 Ω . Therefore, more charges per gram are being gotten, but the transportation or movement of those charges became more challenging. This suggests that the new inorganic phases from the oxides can become obstructive; by interrupting the carbon's conductive paths or adding interfaces where electrons get bogged down. This is in agreement with earlier structural observations, especially from XRD, where

TCGFS was observed to have kept an open, disordered carbon arrangement but became reorganized a bit when the oxides were added. Bottom line, while these oxides can boost activity, when they are present in higher concentrations or get clumped, it unavoidably hurts conductivity and slows down ions [89, 91, 100].

Now, comparing TCGFS with TGFS-1, the latter proved to be better overall: 51.40 F g⁻¹ (CV), 51.73 F g⁻¹ (GCD), and an ESR of 2.58 Ω. Both TCGFS and TGFS-1 started with the same precursor amounts, but TCGFS fell short, and this might be attributable to the lower specific surface area typically associated with restacked rGO sheets, which tends to affect their performance in organic electrolytes if not modified or optimized [63, 77, 161]. More importantly, this shows how much the carbon support matters. TD-C₂TrGO₄'s more defective, disorderly carbon makes a good anchoring surface for oxides but appears to form less efficient conductive networks in the final composite, even as it did not perform well electrochemically in comparison with TD-GLC₃. On the other hand, TGFS-1's GLC-derived structure, with its balance of defects and connectivity, handles the oxide integration much better.

Table 40. Specific capacitance and equivalent series resistance of TD-C₂TrGO₄, TCGFS, and TGFS nanocomposites in TEABF₄/acetonitrile electrolyte.

Sample	CV (C _s / F g ⁻¹)	GCD (C _s / F g ⁻¹)	ESR (Ω)
TD-C ₂ TrGO ₄	33.49	16.84	2.94
TCGFS	28.3	25.0	9.32
TGFS-1	51.40	51.73	2.58

Overall, the electrochemical profile of TCGFS comes down to a mix of carbon structure, how the added oxides spread out, and the resistance at interfaces. It can be concluded that the presence of Fe₂O₃/Fe₃O₄-SiO₂ as part of the composite material helped the GCD capacitance compared to TD-C₂TrGO₄, but the recorded higher ESR may have been a limitation to the overall performance.

These results highlight the fact that the benefit of metal oxide introduction is very sensitive to the carbon support and electrolyte environment, as an identical inorganic phase can give opposing electrochemical responses depending on active site versus conductivity versus ion accessibility trade-offs.

4.6. How the Chapter 4 Outcomes Addressed the Research Objectives

To sum up this chapter, the predetermined synthesis routes highlighted in the objectives of this research were covered, with each synthesis route illustrating how the materials developed as conditions were varied. The chapter began with the production of graphene-like carbon from hazelnut shells. When the three profiles of residence were compared, it was evident that some synthesis conditions more closely favored structural order and others electrochemical activity. This comparison early on showed that mere structural perfection does not ensure good performance. It also provided the residence time baseline for the subsequent optimization.

The Taguchi design was built on that baseline. By varying particle size, catalyst dosage, activation intensity, and pyrolysis temperature, the study identified the combination that produced a carbon with both strong structural features and reliable electrochemical behavior. The optimized sample did not emerge from a single dominant factor but from the interaction of several factors. It became the reference point for the rest of the chapter.

For the oxidation and reduction of the biographite that was used, the oxidation section examined how biographite responds to two different chemical environments. GO-OPT and B-GO were produced from the same precursor but behaved like different materials. GO-OPT carried inorganic residues that influenced its thermal and structural behavior, while B-GO remained closer to a carbon-rich framework that exhibited premature reduction features. The observed contrasts were

very relevant to the outcomes of the reduction processes of GO-OPT, because they set the structural, morphological, and chemical baseline for the reduction that followed. Reduction was explored through chemical, thermal, and sequential routes. Each pathway altered the carbon differently. Chemical reduction removed oxygen aggressively but introduced disorder. Thermal reduction restored some graphitic features without fully eliminating defects. Sequential reduction combined both effects but did not outperform thermal treatment alone. The reduced materials specifically showed that oxygen removal and structural restoration do not proceed in parallel, and that the features of the final carbon that is obtained are dictated by the reducing environment.

Doping introduced another layer of modification. The hydrothermal route produced the most structurally coherent and electrochemically capable doped carbon, with HD-GLC7 standing out as the strongest performer. It was also established that the samples doped using the thermal method did not surpass that of hydrothermal samples, but they have higher levels of defects and sulfur content, along with clear advantages for large-scale manufacturing. For these reasons, TD-GLC₃ sample was selected for the preparation of the composite materials, rather than the independent electrode with the optimal performance. In the subsequently prepared Fe₂O₃/Fe₃O₄ and SiO₂ thermally doped carbon nanocomposites, independent oxide phases were detected using XRD but not identified with advanced characterization like XPS due to constraints. The decline in the performance of the resulting nanocomposites in comparison with the parent material (TD-GLC₃) in TEABF₄/ACN aligns with established patterns, and the findings can provide a meaningful basis for future studies on the interaction between defect-rich carbon and inorganic phases. Comparing TGFS-1 derived from TD-GLC₃ to the nanocomposite made using TD-CTrGO₄ (TCGFS), it was established that the surface-area advantage that the GLC pathway had over the RGO pathway was

reflected again in the electrochemical performance, even as TCGFS indicated higher presence of the oxide phases via XRD and an increase in Fe and S presence in the EDX analysis

Across all sections, Chapter 4 shows how biomass-derived carbon responds to thermal treatment, oxidation, reduction, doping, and composite formation. Each route yielded materials with its own structural and electrochemical property, shaped by the defects, functional groups, and—in the ternary composite pathway—the distribution of oxide phases. The chapter does not present a single best material; instead, it documents how each synthesis decision shapes the carbon and what those changes mean for future applications. Altogether, this gives the experimental applied basis that is required to comprehend the merits, shortcomings, and also potentials of biomass-derived graphene as well as its derivatives.

The results in Chapter 4 showed that each stage of the work tackled the objectives laid out at the start of this dissertation. The synthesis routes, the structural changes they caused, and the electrochemical results all answered the research questions while testing the hypothesis in real terms. With these clear outcomes, the next chapter ties everything together, highlighting the broader significance of the findings, the contributions made, and where they guide future efforts.

5. CONCLUSION

This dissertation set out to explore whether biomass could be pushed, shaped, and refined into graphene-based materials capable of meaningful electrochemical performance. The work did not follow a single straight path, and the results did not converge toward one universal “best” material. Instead, the study uncovered how different synthesis choices pull the carbon in different directions, and how those directions matter for real applications.

The first major contribution of this research is the establishment of a complete, experimentally validated route for producing graphene-like carbon from hazelnut shells. The optimized pyrolysis pathway did not emerge from theory but from careful comparison and statistical tuning. It demonstrated that biomass can be converted into partially graphitic, hierarchically porous carbon using accessible catalysts and activation agents. More importantly, it showed that the most structurally ordered carbon is not necessarily the most electrochemically capable. This insight is essential for future biomass-derived carbon research, where structural perfection is often assumed to be the goal.

The second contribution lies in the oxidation and reduction work. By comparing two oxidation environments and three reduction pathways, the study revealed how sensitive biographite is to chemical treatment. GO-OPT and B-GO behaved like fundamentally different materials, even though they were produced from the same precursor. Their reduction products showed that oxygen removal and structural restoration are not synchronized processes. This understanding is valuable because GO and rGO are often treated as predictable materials; here, they proved to be anything but. The work clarifies how biomass-derived GO responds to chemical stress and where its limitations lie.

The third contribution concerns heteroatom doping. Hydrothermal doping produced the strongest structural and electrochemical improvements, with HD-GLC7 standing out as the most balanced material in the entire study. Thermal doping, although less impressive in performance, offered something the hydrothermal route could not: scalability. TD-GLC3 became the practical choice for downstream work not because it excelled electrochemically, but because it could be produced more easily and modified more aggressively. This distinction between “best performer” and “best platform” is an important outcome of the research.

The fourth contribution comes from the nanocomposite investigation. The composites did not improve capacitance in the tested electrolyte, and the study does not hide that fact. Instead, it explains why. Metal-oxide systems often struggle in organic electrolytes, and the TGFS composites behaved exactly as such systems typically do. Even so, the composites provided structural insight into how inorganic phases interact with defect-rich carbon. They also demonstrated that a drop in performance can serve as a useful diagnostic tool rather than discouraging, highlighting the way the choice of electrolyte can ultimately dictate material design.

Altogether, these findings tell a consistent story. Biomass-derived graphene is not a single material but a landscape of possibilities. Some routes favor conductivity, others favor chemical activity, others favor structural stability. This dissertation mapped that landscape experimentally. It delivered optimized synthesis routes for graphene-like carbon and graphene oxide, identified the most effective doping strategy, and produced nanocomposites that clarified the limits of the chosen electrolyte system. The work does not claim universal improvement; it claims understanding — and that understanding is the foundation on which better materials can be built.

Future work can build on these findings by exploring electrolytes more compatible with metal-oxide composites, pushing hydrothermal doping toward scalable formats, and integrating

the optimized carbon frameworks into full device architectures. The materials developed here are not final answers. Each stage of this work, systematically uncovers something about how biomass carbon behaves under distinct processing conditions. This fundamental understanding is the core contribution of this work, offering a framework that remains applicable beyond these specific materials.

6. LITERATURE

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7. LIST OF SYMBOLS

Abbreviations

ACN	Acetonitrile
ANOVA	Analysis of variance
BET	Brunauer–Emmett–Teller
B-GO	Boric acid-assisted graphene oxide
CA-GLC	Catalytically activated graphene-like carbon
CHNS	Carbon, hydrogen, nitrogen, and sulfur elemental analysis
CO	Carbon monoxide
CO ₂	Carbon dioxide
CoFe ₂ O ₄	Cobalt ferrite
C ₆ H ₈ O ₆	Ascorbic acid
CrGO	Chemically reduced graphene oxide
CTrGO	Sequentially chemically and thermally reduced graphene oxide
CV	Cyclic voltammetry
DOF	Degrees of freedom
EDLC	Electric double-layer capacitance / electric double-layer capacitor
EDTA / EDTA-Na ₂	Ethylenediaminetetraacetic acid / disodium ethylenedetraacetate

EDX / EDS	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
ESR	Equivalent series resistance
FCET	Faculty of Chemical Engineering and Technology
FE-SEM	Field-emission scanning electron microscopy
$\text{Fe}(\text{C}_5\text{H}_5)_2$	Ferrocene
$\text{Fe}^{2+} / \text{Fe}^{3+}$	Iron ions / oxidation states
Fe_3C	Iron carbide (cementite)
FeCl_3	Ferric chloride
$\text{Fe}_2\text{O}_3 / \alpha\text{-Fe}_2\text{O}_3$	Iron(III) oxide / hematite
Fe_3O_4	Iron(II,III) oxide (magnetite)
FTIR	Fourier-transform infrared spectroscopy
GCD	Galvanostatic charge–discharge
GLC	Graphene-like carbon
GLC-OPT	Optimized graphene-like carbon
GO	Graphene oxide
GO-OPT	Optimized graphene oxide
GRA	Grey relational analysis

GRC	Grey relational coefficient
GRG	Grey relational grade
HCl	Hydrochloric acid
H ₂	Hydrogen gas
H ₂ O	Water
H ₂ O ₂	Hydrogen peroxide
H ₂ SO ₄	Sulfuric acid
H ₃ BO ₃	Boric acid
H ₃ PO ₄	Phosphoric acid
HD	Hydrothermal doping
HD-GLC / HD-GLC-i	Hydrothermally doped graphene-like carbon
HC-AC	Hydrothermal carbon activated carbon
HRTEM	High-resolution transmission electron microscopy
HTC	Hydrothermal carbon / hydrochar
HTC-AC	Hydrothermal carbon activated carbon
HTC-PA	Phosphoric acid-activated hydrochar
HTC-PA-Fe / Fe-AC	Fe-reconstructed phosphoric acid-activated hydrochar

HTC-PA-ZnFe / P-TCH	ZnCl ₂ -assisted Fe-reconstructed phosphoric acid-activated hydrochar
IRB	Institute Ruđer Bošković
IRCBM	Interdisciplinary Research Centre in Biomedical Materials
KI	National Chemistry Institute, Slovenia
KMnO ₄	Potassium permanganate
KOH	Potassium hydroxide
MnO ₂	Manganese dioxide
N ₂	Nitrogen gas
N ₂ H ₄	Hydrazine hydrate
Na ₂ SO ₄	Sodium sulfate
NaBH ₄	Sodium borohydride
NaNO ₃	Sodium nitrate
NCP	National Centre for Physics
NH ₂ CSNH ₂	Thiourea
NLPDFT	Non-local density functional theory
NMP	N-methyl-2-pyrrolidone
NO ₂ / N ₂ O ₄ / NO _x	Nitrogen oxide species
PVDF	Polyvinylidene fluoride

rGO	Reduced graphene oxide
SA-GLC	Simultaneously activated graphene-like carbon
SEM	Scanning electron microscopy
SiO ₂	Silicon dioxide
STEM	Scanning transmission electron microscopy
TCGFS	Thermally doped combined chemically and thermally reduced graphene oxide with iron oxide and SiO ₂ nanocomposite
TD	Thermal doping
TD-CTrGO / TD-CTrGO _i	Thermally doped sequentially reduced graphene oxide
TD-GLC / TD-GLC _i	Thermally doped graphene-like carbon
TEABF ₄ /ACN	Tetraethylammonium tetrafluoroborate in acetonitrile
TEM	Transmission electron microscopy
TGFS	Iron oxide–silica nanocomposite on thermally doped carbon
TGFS-1/TGFS-2/TGFS-3	Thermally doped graphene-like carbon with iron oxide and SiO ₂ nanocomposites
TGA	Thermogravimetric analysis
TiO ₂	Titanium dioxide
TrGO	Thermally reduced graphene oxide
XPS	X-ray photoelectron spectroscopy

XRD	X-ray diffraction
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ZnCl ₂	Zinc chloride
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ZnO	Zinc oxide
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Symbols

2θ	Diffraction angle in XRD
C_{device}	Full-device specific capacitance
C_s	Specific capacitance
d_{002}	Interlayer spacing corresponding to the (002) crystallographic plane
E	Specific energy density
I	Current / discharge current
I_D/I_G	Intensity ratio of Raman D-band to G-band
I_{2D}/I_G	Intensity ratio of Raman 2D-band to G-band
L_a	In-plane graphitic crystallite/grain size
L_c	Crystallite height/stacking size
m	Active material mass
N_{sheet}	Number of stacked graphene sheets
O/C	Oxygen-to-carbon atomic ratio
P	Specific power density
V	Voltage / practical operating voltage window
w/w	Weight-to-weight ratio
wt%	Weight percent

$(001), (002), (100)$	Miller indices for crystallographic planes
Δt	Discharge time
ΔV	Operating/discharge voltage window
ν	Scan rate

8. APPENDICES

APPENDIX 1. TABLES

Table A1. Analysis of variance (ANOVA) results for the four evaluated response factors (Yield, BET surface area, I_D/I_G ratio, and TGA mass retention). The KOH/Biochar ratio (factor B) exhibited the highest contribution to the model and was statistically significant ($p < 0.05$) across all responses.

Response Factor	Source	SS	df	MS	F-Value	p-Value	Contribution
Yield (g)	Model	3.674	–	0.916	62.91	0.0007	Significant
	B: KOH/Biochar ratio	2.532	1	2.786	6.90	0.0005	Primary
	C: Ferrocene dose	1.132	2	0.567	38.93	0.0024	Secondary
BET Surface Area ($\text{m}^2 \text{g}^{-1}$)	Model	1.081 $\times 10^6$	2	5.403 $\times 10^5$	11.51	0.0088	Significant
	B: KOH/Biochar ratio	1.081	2	5.403 $\times 10^5$	11.51	0.0088	Primary
I_D/I_G Ratio	Model	0.2985	2	0.1492	5.28	0.0475	Significant
	B: KOH/Biochar ratio	0.2985	2	0.1492	5.28	0.0475	Primary
TGA Mass Retention (%)	Model	172.67	2	86.33	11.43	0.0090	Significant
	B: KOH/Biochar ratio	172.67	2	86.33	11.43	0.0090	Primary

APPENDIX 2. FIGURES

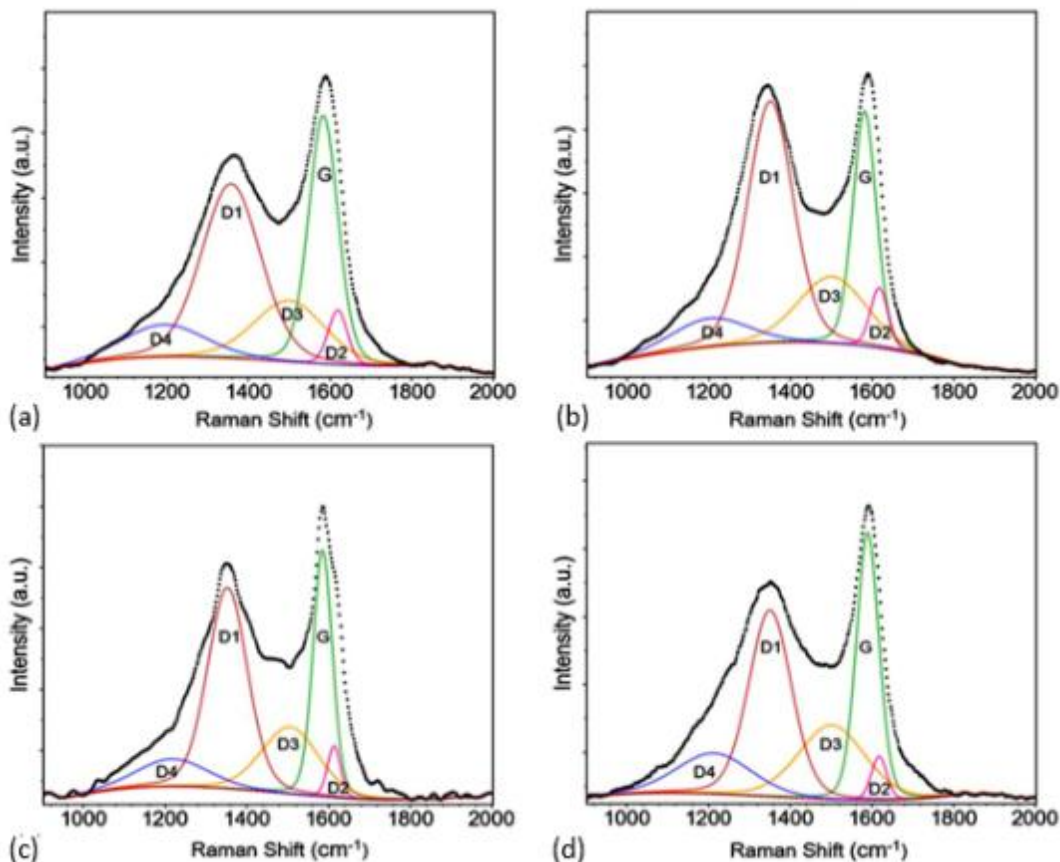


Figure A1. Deconvoluted Raman spectra showing the D1, D2, D3, D4, and G components for (a) HTC, (b) HTC-PA, (c) HTC-PA-Fe, and (d) HTC-PA-ZnFe.

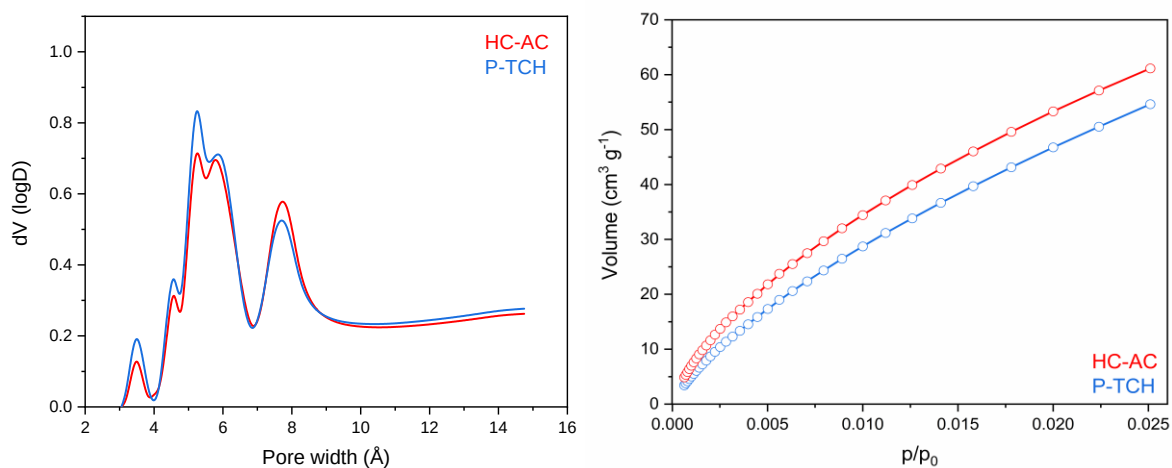


Figure. A2. NLDFT pore size distribution profiles and corresponding NLDFT fit curves derived from CO₂ sorption isotherms measured at 0°C for the investigated materials (measured data – circles, fitted data – full lines) for HTC-PA (HC-AC) and HTC-PA-ZnFe (P-TCH).

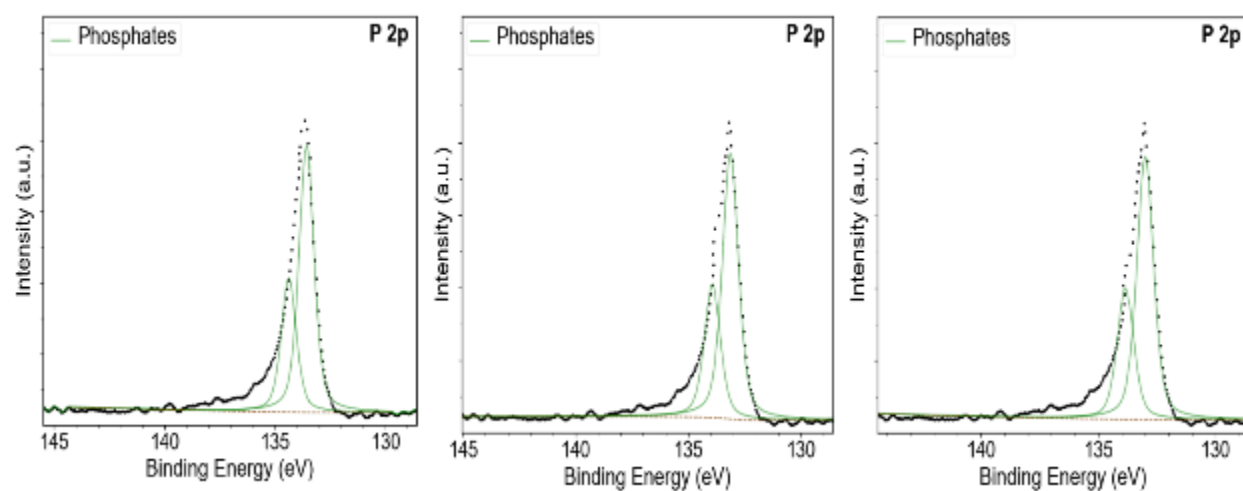


Figure A3. High-resolution P 2p XPS spectra of (a) HTC-PA, (b) HTC-PA-Fe, and (c) HTC-PA-ZnFe, showing peak deconvolution into phosphorus-containing bonding environments.

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