



**GRAPHENE AND ITS DERIVATIVES FOR ENERGY STORAGE
AND ENVIRONMENTAL REMEDIATION**

Thesis submitted in partial fulfillment of the requirements for the degree

of

Doctor of Philosophy

by

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**GRAPHENE AND ITS DERIVATIVES FOR ENERGY STORAGE
AND ENVIRONMENTAL REMEDIATION**

by

SURAJ KUMAR

and

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Submitted

In partial fulfillment of the requirements for the degree

of

DOCTOR OF PHILOSOPHY IN CHEMISTRY

OF

NAGALAND UNIVERSITY

Dedicated to my family

My beloved parents

Mom (Teatar Devi) and Dad (Shree Ram Das)

My sister

Suman Kumari

and

My brothers

Suresh Kumar and Bibek Kumar

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To the best of my knowledge, the work embodied in this thesis is original and has not been submitted previously, either wholly or in part, to any other University or Institution for the award of any degree or diploma.

The thesis is therefore recommended for evaluation and consideration for the award of the Ph.D. degree in Chemistry by Nagaland University.

I appreciate his sincere efforts, dedication, and perseverance in successfully completing this research work and wish him success in all his future academic and professional pursuits.

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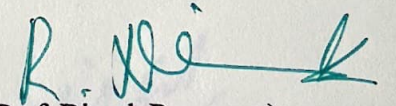
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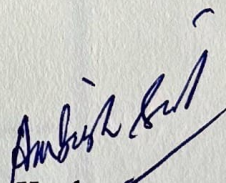
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I, **Mr. Suraj Kumar**, hereby declare that the subject matter of this Thesis is the record of work done by me, that the contents of this Thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/Institute.

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(SURAJ KUMAR)

ABSTRACT

The growing global demand for sustainable energy storage systems and environmental remediation technologies necessitates the development of advanced carbon-based materials with tuneable physicochemical properties. In this thesis, graphene-based materials were systematically engineered through theoretical design and green chemical functionalization strategies to enhance their structural, electronic, electrochemical, and adsorption characteristics for multifunctional applications.

The study began with a density functional theory (DFT) investigation of platinum group element (Ru, Rh, Pd, Os, Ir, and Pt) doped graphene to understand the influence of metal incorporation on structural stability, electronic structure, optical response, and charge distribution. Calculations performed at the B3PW91/LANL2DZ level revealed that PGE doping significantly modulates the HOMO–LUMO gap, density of states, and optical absorption behavior, indicating strong potential for applications in optoelectronics, sensing, and energy devices.

Building upon theoretical insights, a rapid and scalable synthetic strategy was developed for the preparation of aminated reduced graphene oxide (NH₂-rGO). The process was completed within ~9 h under moderate conditions, achieving tunable nitrogen incorporation (2–6%). The functionalized material exhibited significantly enhanced wettability and electrochemical activity. A symmetric supercapacitor fabricated using NH₂-rGO delivered a high specific capacitance of 322 F g⁻¹ and a markedly improved volumetric energy density, demonstrating the effectiveness of nitrogen functionalization in enhancing charge storage performance.

To further expand the functionalization landscape, a green and rapid bromination methodology for rGO was established using tribromide reagents. In the first approach, efficient bromination was achieved via reflux within one hour, enabling tunable bromine incorporation (0.43–4.73%) while avoiding toxic reagents and harsh conditions. The resulting bromographene-based symmetric supercapacitor exhibited a wide 3 V potential window and delivered an energy density of 46.44 Wh kg⁻¹, significantly higher than non-brominated counterparts.

Subsequently, a systematic comparative investigation of five quaternary ammonium tribromides: tetraethylammonium, tetrapropylammonium, tetrabutylammonium, cetyltrimethylammonium, and cetylpyridinium tribromides, was conducted to evaluate bromination efficiency and structural impact. XPS, FTIR, XRD, and FESEM analyses confirmed bromine incorporation up to ~9.4 at%. Notably, certain tribromides simultaneously introduced nitrogen functionalities, enabling dual heteroatom incorporation under mild, low-temperature conditions. The generated C–Br functionalities provide reactive platforms for further substitution and derivative synthesis.

Finally, leveraging the synergistic advantages of nitrogen and bromine functionalities, a dual-functionalized graphene (DFG) was engineered to enhance conductivity, interfacial charge transport, and redox activity. The resulting DFG demonstrated reduced charge-transfer resistance and superior electrochemical performance. A symmetric 3.2 V supercapacitor device delivered high energy density (60.89 Wh kg^{-1}), excellent cycling stability (98.81% retention after 10,000 cycles), and reliable operation over a wide temperature range (-15 to $100 \text{ }^{\circ}\text{C}$). Practical feasibility was validated through regenerative braking energy capture in an electric vehicle prototype, highlighting its potential for automotive applications.

Beyond energy storage, the adsorption performance of aminated graphene toward polycyclic aromatic hydrocarbons was investigated using naphthalene as a model pollutant. Tunable amine-functionalized samples exhibited high adsorption capacity (144.65 mg g^{-1}), following pseudo-second-order kinetics and Langmuir isotherm behavior. Complementary DFT studies revealed enhanced binding interactions through π – π stacking, electron donor–acceptor interactions, and hydrogen bonding, demonstrating the dual role of functionalization in both energy and environmental applications.

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Chapter

1

Introduction and literature
review

CHAPTER 1

Introduction

1.1 Background

The 21st century is facing serious challenges related to energy demand and environmental sustainability [1]. Due to rapid population growth, industrial development, urbanization, and technological progress, the global demand for energy has increased significantly [2,3]. At the same time, these developments have also led to increased environmental pollution and resource depletion [4]. Addressing these twin challenges together in a sustainable, cost-effective, and environmentally friendly way has become one of the most important scientific and technological goals of the present century.

Global energy demand has increased steadily over the past few decades and is projected to continue rising due to population growth, electrification of transportation, digital infrastructure expansion, and industrial development [5]. While renewable energy technologies such as solar and wind power offer sustainable alternatives to fossil fuels, their intermittent and variable nature presents significant challenges for grid stability and energy reliability [1]. Thus, there is an urgent requirement to develop advanced energy storage systems (ESS) that can supply energy whenever needed. The performance characteristics of various ESS are commonly illustrated using a Ragone plot, which correlates energy density with power density (Figure 1.1) [6]. At the forefront of these ESS are batteries and supercapacitors (SCs). Batteries have traditionally been the most widely used energy storage technology in several applications ranging from power backup systems, to portable electronic gadgets. However, in recent years, supercapacitors have gained significant interest among researchers and have emerged as a promising advancement in energy storage technology [6].

A supercapacitor (SC), similar to a battery, is an electrochemical device designed to store and deliver electrical energy. The general structure of a supercapacitor is comparable to that of a battery, consisting of two electrodes separated by an electrolyte-filled separator [7]. However, unlike conventional batteries, which store energy through chemical reactions involving redox processes, supercapacitors primarily store energy through electrostatic charge accumulation at the electrode

electrolyte interface. As a result, batteries generally require longer charging times and undergo irreversible electrochemical changes during repeated charge–discharge cycles, which gradually reduce their energy density and shorten their lifespan [7]. In contrast, supercapacitors provide rapid charging and discharging capability (high power density) along with outstanding cycle stability and long operational life. As illustrated in Figure 1.1, supercapacitors occupy the intermediate region between traditional capacitors and batteries. Despite their many advantages, the energy density (*i.e.* their ability to store charge/energy) of currently available supercapacitors, remains relatively low. Commercial supercapacitors typically exhibit energy densities around 10 Wh kg^{-1} , whereas lead–acid batteries provide higher values in the range of $20\text{--}35 \text{ Wh kg}^{-1}$. Furthermore, modern lithium-ion batteries can achieve energy densities of approximately 150 Wh kg^{-1} [8]. Therefore, enhancing the energy density of supercapacitors while maintaining high power density and long cycling stability remains a major research challenge [6,8].

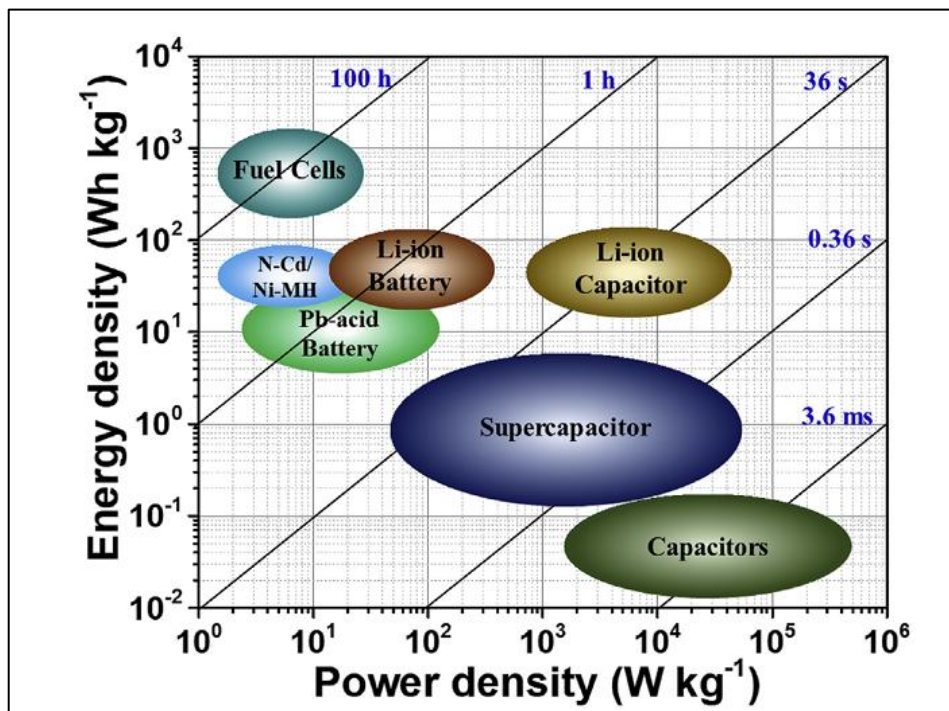


Figure 1.1. Ragone plot of different energy storage devices. Reproduced with permission from Ref. [9].

Currently, most commercial SCs employ activated carbon as the electrode material due to its high specific surface area, good electrical conductivity, chemical stability,

and cost-effectiveness [10]. However, the presence of poorly interconnected porous structures in activated carbon restricts efficient ion transport, resulting in a specific capacitance typically below 150 F g^{-1} and consequently a low energy density of around 5 Wh kg^{-1} [11,12]. This limitation has driven the development of alternative SC electrode materials over the past two decades.

Further, the energy density (E) of a supercapacitor is governed by the relationship:

$$E = \frac{1}{2} C_{SP} V^2 \quad (1.1)$$

where C_{SP} represents the specific capacitance and V denotes the operating voltage window of the device. According to this relationship, energy density increases linearly with capacitance but increases quadratically with the voltage window. Therefore, expanding the operational voltage range is considered one of the most effective strategies for improving the overall energy density of supercapacitors. However, the voltage window is often limited by electrolyte decomposition and electrode stability. For instance, aqueous electrolytes typically allow a voltage window of approximately 1.0–1.2 V, whereas organic electrolytes can extend the window to about 2.5–3.0 V, albeit with increased cost and safety concerns [6,13]. More recently, ionic liquid electrolytes have attracted attention due to their ability to operate at voltages exceeding 3 V, although challenges related to viscosity, ionic conductivity, and cost remain.

Therefore, enhancing the energy density of supercapacitors requires a synergistic strategy involving both electrolyte engineering and the development of advanced electrode materials with superior capacitance and structural stability. Among the various electrode materials investigated, graphene has emerged as a highly promising candidate due to its exceptional physicochemical properties [14]. Graphene possesses an ultrahigh theoretical surface area ($\sim 2630 \text{ m}^2 \text{ g}^{-1}$), excellent electrical conductivity, mechanical robustness, and tunable surface chemistry, making it highly suitable for facilitating rapid electron transport and efficient ion adsorption [14].

However, pristine graphene often suffers from sheet restacking caused by strong π – π interactions, which reduces the accessible surface area and limits electrochemical

performance. To overcome these challenges, rational surface functionalization of graphene derivatives has been widely explored as an effective materials engineering strategy [13]. Functionalization introduces surface functional groups that not only prevent graphene agglomeration but also generate additional electrochemically active sites, improve electrolyte wettability, and enhance charge transfer kinetics at the electrode–electrolyte interface [13]. Thus, graphene-based materials offer a promising pathway for improving supercapacitor performance. The research presented in this thesis focuses on the development of functionalized graphene-based electrode materials combined with ionic liquid electrolytes to achieve enhanced electrochemical performance and wider operating voltage windows.

Alongside the growing energy crisis, environmental pollution, particularly water contamination, has emerged as another global threat [4]. Water is vital for human life. Even though many efforts have been made to reduce pollution, water pollution remains a serious threat to human health. This problem has become worse with rapid economic growth around the world [15]. Over the past 100 years, global water use has increased by about 600% and continues to rise each year with an annual increment rate of 1.8% [4]. Industrial activities, agriculture, and urban development have damaged the environment and polluted important water bodies such as rivers and oceans. This pollution harms ecosystems and directly affects human health and sustainable social development. Globally, nearly 80% of industrial and municipal wastewater is released into the environment without proper treatment. The situation is more severe in least developed countries, where sanitation and wastewater treatment systems are inadequate or absent [16]. Globally, an estimated 2.2 billion people (roughly one in four) still lack access to safely managed drinking water services, forcing many to rely on unsafe or untreated water sources that are vulnerable to contamination from pathogens and chemical pollutants. Unsafe water and inadequate sanitation account for approximately 3.7% of the global annual disease burden.

To address water contamination, various pollutant removal strategies have been developed, including biodegradation, photocatalysis, membrane filtration, advanced

oxidation processes, and adsorption [17]. The advantages and limitations associated with these techniques are discussed in Table 1.1.

Table 1.1: Comparative Overview of Pollutant Removal Methods.

Methods	Advantages	Disadvantages	Ref.
Adsorption	High removal efficiency; relatively low processing cost; simple; flexible adsorbent choice; can achieve high removal efficiencies for organic pollutants	Labor-intensive handling; Adsorbent regeneration/disposal issues	[18]
Advanced Oxidation Processes	High removal efficiency; controllable operating conditions	Expensive implementation; potential formation of by-products	[19]
Biodegradation	Cost-effective; environmentally friendly; good for biodegradable organics	Slow process; sensitive to environmental conditions	[20]
Membrane Filtration	High removal efficiency for dissolved pollutants; size-based separation	High capital/operating cost; membrane fouling issues	[20]
Photocatalysis	Uses light energy for degradation; can degrade a wide range of pollutants	Possible formation of toxic intermediates; limited catalyst reuse; efficiency drops under certain conditions; requires light source	[21]

Among the various treatment techniques reported, adsorption is widely regarded as one of the most effective and practical methods for the removal of both organic and inorganic pollutants, from wastewater [18]. Its increasing adoption is primarily attributed to its operational simplicity, relatively low capital and operating costs, and minimal risk of secondary pollution [20]. In addition, adsorption offers high removal efficiency even at low contaminant concentrations and can be readily integrated with existing water treatment systems, making it particularly attractive for large-scale and real-world applications [20]. Traditional adsorbents such as activated carbon have been widely used; however, their performance is often limited by poor regeneration efficiency, reduced selectivity, and gradual loss of adsorption capacity during repeated use cycles.

In recent years, two-dimensional materials, particularly graphene, have attracted considerable attention as next-generation adsorbents owing to their exceptional properties [22]. The ability to tailor their surface chemistry further enhances their versatility for adsorption applications. However, a comprehensive understanding of the adsorption mechanisms and pollutant–surface interactions in graphene-based systems remains limited, thereby presenting significant opportunities for further experimental and theoretical investigation. Despite extensive experimental investigations demonstrating enhanced adsorption performance of graphene-based materials, the fundamental mechanisms governing pollutant–surface interactions remain incompletely understood. Experimental adsorption studies primarily rely on empirical isotherm and kinetic models, which describe macroscopic adsorption behavior but provide limited insight into molecular-level interactions.

To overcome these limitations, theoretical modelling has become an essential tool in modern materials research [23]. Theoretical modelling provides atomic-scale understanding of material behavior by enabling detailed investigation of structural stability, electronic structure, and adsorption interactions. Among the various computational approaches, Density Functional Theory (DFT) has emerged as one of the most widely adopted methods due to its ability to accurately predict electronic and structural properties while maintaining computational efficiency [23].

DFT plays a crucial role in understanding graphene-based systems by enabling evaluation of charge distribution, structural changes and optical properties. Furthermore, DFT calculations provide quantitative insight into adsorption mechanisms by evaluating adsorption energies, charge transfer processes, and molecular interaction configurations between pollutant molecules and graphene surfaces [24]. Therefore, the integration of experimental investigations with theoretical modelling provides the foundation and motivation for the present research work.

The subsequent sections provide a comprehensive discussion of graphene, encompassing its historical development and discovery, various synthesis strategies, derivatives, and its applications in electrochemical energy storage and environmental remediation. Additionally, an introduction to DFT is presented, as it plays a crucial role in understanding the structural, electronic, and adsorption properties of graphene-based systems.

1.2 Graphene: A wonder material

1.2.1 Discovery and history

Materials are essential for the progress of science and technology, as many new technologies depend on the availability of new and improved materials. For this reason, discovering materials with excellent properties has always been an important goal of scientific research. One such material is graphene, which gained major attention after it was first isolated from graphite by Andre Geim and Konstantin Novoselov in 2004. The discovery of graphene marked the start of a new and important phase in materials science research [25].

Graphene is a single, flat layer of carbon atoms arranged in a two-dimensional honeycomb pattern. It is the basic building unit of all graphitic carbon materials. Because of this, graphene is often called the “mother” of all graphitic forms. It can be wrapped to form zero-dimensional (0D) fullerenes, rolled into one-dimensional (1D) nanotubes, or stacked to create three-dimensional (3D) graphite structures (Figure 1.2). Before the discovery of graphene, it was believed that 2D materials were

unstable. Landau and Peierls [26] asserted that 2D materials were thermodynamically unstable and deemed impossible to exist. According to them, thermal fluctuations in such materials would induce atom displacements comparable to interatomic distances at any finite temperature [27]. Mermin [28] extended this argument, and a comprehensive array of experimental observations substantiated its validity. However, this notion was dispelled when Geim and Novoselov discovered graphene in 2004 [29]. Within a short span of weeks, another research group reported the growth of ultrathin graphite films on silicon carbide [30]. These groundbreaking studies directed attention to graphene, marking its significance as the first-ever obtained 2D material and thus, graphene's "gold rush" began [25].

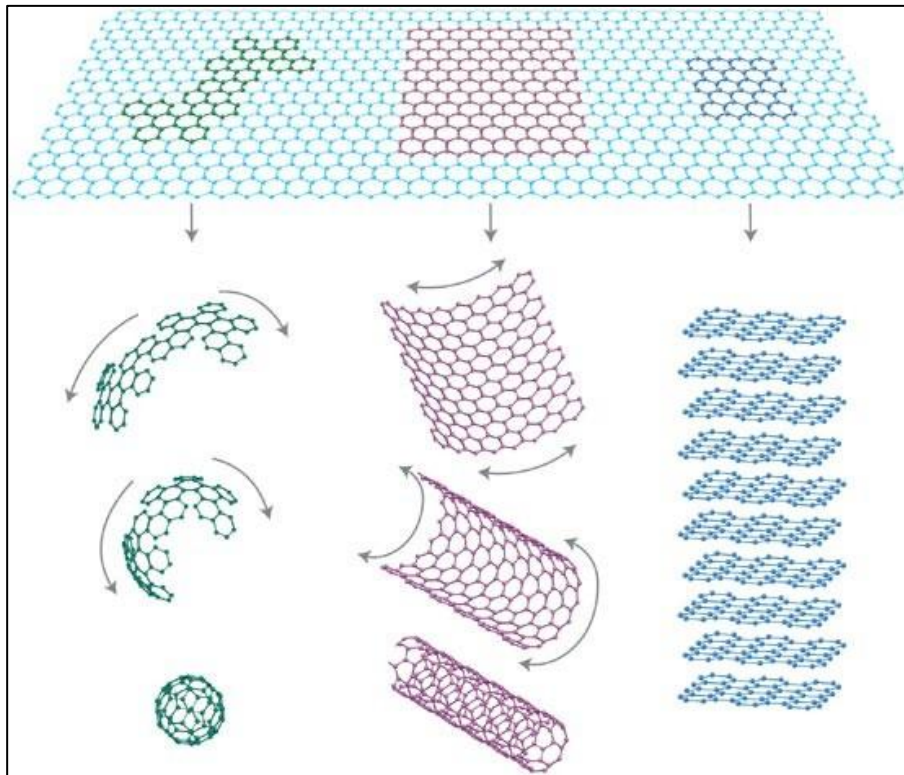


Figure 1.2. Graphene, “Mother of all graphitic forms”. Reproduced with permission from Ref. [25].

The hexagonal geometry of graphene contributes to its structural stability [31]. Each carbon atom is connected to the neighboring carbon atom by sp^2 hybridization, providing a non-bonding electron to create a large π bond that facilitates the free movement of electrons [32]. Graphene also displays an exceptional combination of

numerous superior physical properties such as tensile strength of 125 GPa, excellent carrier mobility of $2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [33,34], thermal conductivity reaching as high as $5.5 \times 10^3 \text{ W m}^{-1} \text{ K}^{-1}$ [35,36] and theoretical surface area of $2630 \text{ m}^2 \text{ g}^{-1}$ [37]. These properties of graphene make it widely applicable in numerous domains, such as spintronics [38], energy storage [39], nanoelectronics [40], wastewater treatment [41], and materials with high thermal conductivity [42].

Although graphene was experimentally isolated only recently, its structure and properties (also referred to as “2D graphite”) have been theoretically studied for more than sixty years and have long been used to explain the behavior of many carbon-based materials [25]. The history of graphene predates its formal identification as a distinct two-dimensional material by more than a century. As explained by Nobel laureate, Prof. Andre Geim in his paper “Graphene Prehistory” [43], early research mainly involved basic observations and did not recognize graphene as a distinct material with its own crystal structure.

The earliest experimental encounter with graphene-related structures can be traced to the work of Benjamin C. Brodie in 1859 [44]. By oxidizing graphite using strong acids, Brodie produced what he termed “carbonic acid.” With the benefit of hindsight, this material can be interpreted as graphene oxide, densely functionalized with oxygen-containing groups, dispersed as microscopic crystallites in solution (Figure 1.3 (a)). However, Brodie neither isolated individual atomic layers nor recognized their two-dimensional nature.

Over the following century, numerous studies examined the laminated structure and chemistry of graphite oxide. The theoretical foundation for graphene’s electronic properties was laid by Wallace in 1947, who developed a tight-binding description of a single hexagonal layer of carbon while analysing the band structure of graphite [45]. By treating the layer as an isolated two-dimensional honeycomb lattice, Wallace demonstrated that the conduction and valence bands meet at the corners of the Brillouin zone, yielding a zero-band gap. Although the relativistic interpretation was not recognized at the time, the linear energy–momentum relation obtained near these band-touching points later became central to the description of charge carriers in

graphene as massless Dirac fermions. Wallace's work therefore provided the essential theoretical framework that enabled interpretation of graphene's electronic behavior following its experimental isolation decades later. A crucial advance came in 1948, when G. Ruess and F. Vogt used transmission electron microscopy to observe thin, crumpled flakes obtained by drying droplets of graphene oxide suspensions [46]. These flakes were only a few nanometres thick, indicating the presence of very thin graphitic sheets, although individual monolayers were not conclusively identified at that time.

A more direct identification of atomically thin carbon layers was reported in 1962 by Hans-Peter Boehm and co-workers [47]. By chemically reducing graphite oxide dispersed in alkaline media, they obtained extremely thin carbon foils and used transmission electron microscopy to estimate their thickness (Figure 1.3 (b)). Some of these foils had thicknesses as low as 3–6 Å, which corresponds to one to a few atomic carbon layers. Consequently, the Boehm–Hofmann work is now regarded as the first experimental observation of graphene sheets, even though their electronic properties were not investigated and the material's significance was not recognized at the time. Furthermore, Hans-Peter Boehm and his colleagues formally coined the term “graphene” in 1986 to describe the then hypothetical single atomic layer of carbon [48]. The name was derived from the word graphite combined with the suffix -ene, which is commonly used for polycyclic aromatic hydrocarbons.

In parallel with chemically derived graphene-like sheets, ultrathin graphitic films were also grown epitaxially on various substrates such as SiC, graphite, Ru, Rh, Ni from the 1970s onward (Figure 1.3 (d)) [49–53]. Further, efforts to make thin films of graphite by mechanical exfoliation can be traced back to the early 1990s [43]. In 1990, Heinrich Kurz and co-workers prepared optically thin graphite films by mechanically peeling layers from highly oriented pyrolytic graphite (HOPG) using transparent adhesive tape [54]. These thin films were subsequently employed to investigate carrier dynamics in graphite. In 1995, Ebbesen and Hiura showed that ultrathin graphitic sheets on HOPG could be mechanically folded and torn in well-defined

crystallographic directions, introducing the concept of “graphite origami” and revealing the remarkable mechanical flexibility of graphene layers [55].

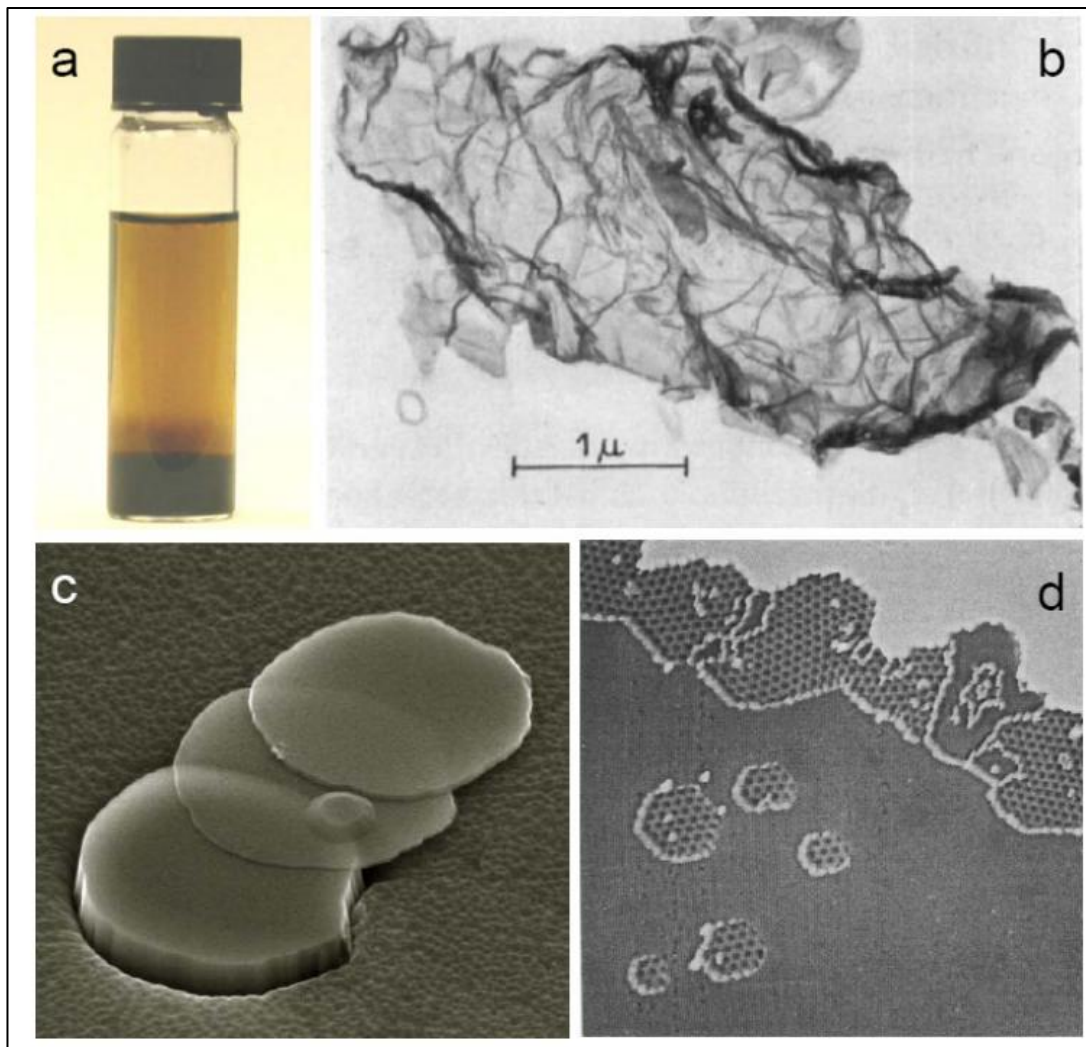


Figure 1.3. (a) Likely early observation by Brodie (~150 years ago), where graphite oxide dispersed in water formed a yellow suspension of floating graphene flakes. (b) TEM image (1960s) showing ultra-thin graphitic flakes. (c) SEM image of thin graphite platelets obtained by mechanical cleavage. (d) STM image ($100 \times 100 \text{ nm}^2$) of graphene grown on Pt. Reproduced with permission from Ref. [43].

Later, Lu et al. (1999) [56] developed a more controlled approach by patterning HOPG into micron-sized graphite islands using oxygen plasma etching, followed by AFM-based manipulation in an effort to peel off single or few-layer sheets (Figure 1.3 (c)). Although these methods did not yet yield large, free-standing graphene monolayers, they clearly demonstrated that mechanical exfoliation of atomically thin graphitic

layers was feasible. In 2003, Yang Gan and co-workers reported the formation of graphene monolayers on HOPG using scanning tunnelling microscopy [57]. By repeatedly scanning the STM tip against step edges on graphite terraces, the topmost graphene layer could be mechanically torn from the surface and folded or rotated relative to the underlying substrate. STM imaging confirmed that only a single atomic layer was detached, and that the rotated monolayer produced characteristic moiré superstructures arising from lattice misorientation.

Finally, the big breakthrough came in 2004 when Andre K. Geim and Konstantin S. Novoselov, together with co-workers, reported the isolation and electronic characterization of atomically thin carbon films [29]. Using repeated mechanical exfoliation of highly oriented pyrolytic graphite, they prepared monocrystalline graphitic sheets with thicknesses down to a single atomic layer and demonstrated that these films were stable under ambient conditions. Devices fabricated from one- to three-layer graphene exhibited metallic conductivity and exceptionally high electronic quality, despite their atomic thickness.

Most importantly, the authors reported a strong ambipolar electric-field effect, in which application of a gate voltage continuously tuned the charge carriers from electrons to holes, with carrier concentrations reaching $\sim 10^{13} \text{ cm}^{-2}$ and room-temperature mobilities of up to $\sim 10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Magneto transport measurements further demonstrated pronounced Shubnikov–de Haas oscillations, establishing that charge transport in these films was strictly two-dimensional and of remarkably high quality.

This work provided the first clear demonstration that a truly two-dimensional crystal could exist in a free, stable form and, crucially, that it possessed electronic properties fundamentally distinct from bulk graphite. By enabling systematic electrical measurements on monolayer and few-layer graphene, the 2004 report transformed earlier observational studies into a new field of two-dimensional electronics and marked the beginning of modern graphene research. In recognition of this groundbreaking work, Andre K. Geim and Konstantin S. Novoselov were awarded the

Nobel Prize in Physics in 2010 “for groundbreaking experiments regarding the two-dimensional material graphene” [25,43].

1.2.2 Synthesis of graphene

Graphene synthesis methods are broadly categorized into two approaches based on the starting materials: top-down and bottom-up. Top-down methods utilize graphite as the parent material, focusing on overcoming the van der Waals forces between graphene layers to isolate monolayer or few-layer graphene flakes. In contrast, bottom-up methods employ various carbonaceous precursors, where high-energy processes decompose the precursors and graphitize the resulting carbon to form graphene. Figure 1.4 provides an overview of the reported methodologies for graphene synthesis.

Mechanical exfoliation

Mechanical exfoliation, also known as the scotch tape or peel-off technique, was first introduced by Novoselov and Geim in 2004 for fabricating single-layer graphene [29]. This method utilises mechanical force to detach thin layers from a bulk crystal, mostly employing adhesive tape as the tool. A bulk graphite material is positioned on the tape, and through continuous folding, pressing, and peeling, the graphite layers are reduced to produce ultrathin graphene flakes. The last peeling with fresh tape segregates flakes of diverse sizes and thicknesses [58–60]. This technique is exceptionally efficient for generating ultrathin, highly crystalline graphene with few defects, rendering it a dependable method for synthesising research-grade materials. Nonetheless, it poses obstacles for large-scale production due to its sluggish, labour-intensive characteristics and the difficulty in regulating the thickness of the flakes. Consequently, mechanical exfoliation is predominantly employed for the investigation of graphene's characteristics rather than for commercial purposes [59].

Oxidation exfoliation-reduction

Graphene can be synthesized on a large scale through the reduction of graphene oxide (GO), a widely adopted process due to its cost-effectiveness and high yield [61]. This process involves the oxidative exfoliation of graphite to produce GO, which is subsequently reduced to prepare rGO. The preparation of GO serves as a critical step

in this method. GO is synthesized using strong acids and oxidants such as sulfuric acid, nitric acid, and potassium permanganate. Several classical approaches to GO synthesis include the Brodie, Staudenmaier, and Hummer's methods, each offering unique advantages and limitations. The Brodie method (1859) employed potassium chlorate in a graphite slurry with fuming nitric acid, producing GO through multiple steps [62]. The process was later refined by the Staudenmaier method (1898), which integrated concentrated sulfuric acid to yield highly oxidized GO in a single step [63]. The widely used Hummer's method (1958) eliminated the use of hazardous nitric acid and employed sodium nitrate, sulfuric acid, and potassium permanganate, making the process safer and more efficient [61]. Modern modifications to the Hummer's method, such as the Marcano improvement [64], have enhanced oxidation efficiency by excluding NaNO_3 and using a mixture of sulfuric acid and phosphoric acid. During oxidation, the interlayer spacing of graphite increases significantly, from approximately 0.335 nm in pristine graphite to around 0.625–0.735 nm in GO, depending on oxidation time. The exfoliation of GO into individual layers is achieved by ultrasonication in solvents like water, dimethylformamide (DMF), or ethylene glycol, forming well-dispersed suspensions.

To convert GO into graphene or rGO, a variety of reducing agents and methods are employed, each tailored to specific applications and material properties. Among these, chemical reduction is the most widely used approach due to its simplicity and effectiveness. This process involves the use of reducing agents such as hydrazine hydrate, sodium borohydride, ascorbic acid [65]. Hydrazine, despite being effective, is toxic and costly, prompting the exploration of greener alternatives, including amino acids, plant-based reductants, and hydroquinone. Other reducing methods include electrochemical, thermal, hydrothermal, and microwave-assisted reductions, which address concerns about toxicity and energy consumption [66–68].

Chemical vapour deposition

The chemical vapor deposition (CVD) technique is widely regarded as an efficient bottom-up approach for synthesizing high-quality graphene at a large scale [69].

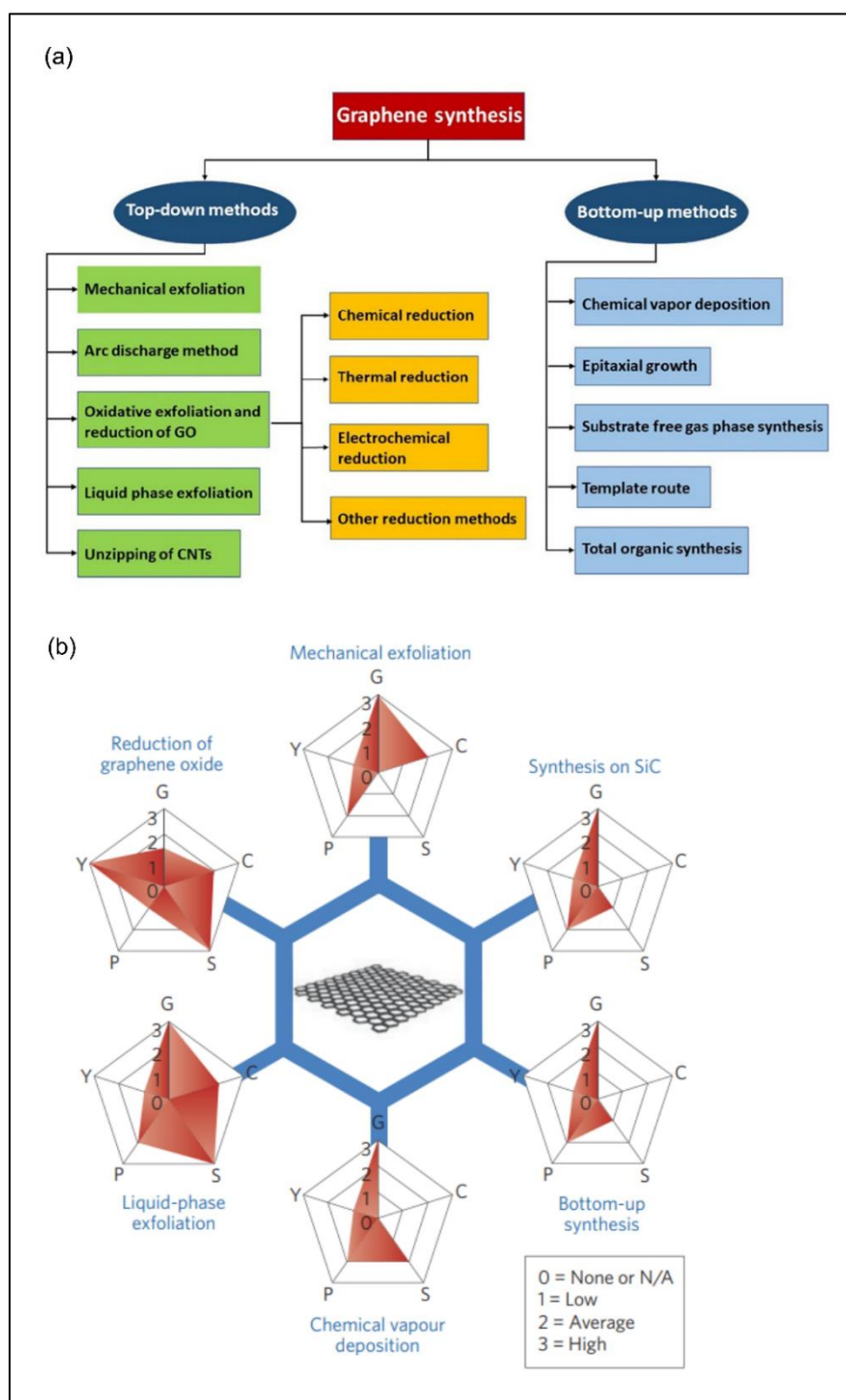


Figure 1.4. (a) Illustration of the various synthesis routes for graphene preparation. (b) Evaluation based on graphene quality (G), cost (C; lower values indicate higher production cost), scalability (S), purity (P), and overall production yield (Y). Reproduced with permission from Ref. [70,71].

It involves the decomposition of precursors in a controlled environment to deposit carbon atoms onto a substrate, forming graphene films. The process takes place in a reaction chamber under specific conditions of temperature, pressure, and gas flow. A typical CVD setup includes a quartz reaction chamber, mass flow controllers, a vacuum pump, temperature measurement tools, and an automated control system [72]. Different substrates are used in CVD for graphene film growth. Common substrates for graphene growth includes nickel, copper, iron, and stainless steel [73]. These materials serve as catalysts for the decomposition of hydrocarbon gases like methane, acetylene, ethylene, or biomass-derived materials [74–77]. Among these, copper and nickel are the most frequently used due to their catalytic properties. The concept of using CVD for graphene synthesis was introduced in 2006 by Somani and colleagues [78] who proposed applying the technique in a manner similar to its use in nanotube synthesis. In their approach, they utilized camphor as the precursor material and nickel substrates for carbon deposition, leading to the formation of ‘planar few-layer graphene’, which consisted of ~ 35 graphitic layers. This initial attempt sparked further research and advancements in refining the CVD process for graphene production.

In the following years, several groups sought to improve the quality and scalability of graphene production. In 2008, Yu et al. [79] used Ni foils and CH_4 , discovering that the cooling rate and hydrogen annealing were crucial for enhancing graphene quality. By 2009, multiple groups independently explored atmospheric pressure CVD using Ni films and Si/SiO₂ substrates, demonstrating the potential for fabricating devices such as field-effect transistors [34,80]. These studies revealed that thinner Ni substrates and shorter growth times favoured the formation of mono- and bilayer graphene. At the same time, large-area, high-quality graphene was synthesized on copper foils, where the process was found to be self-limiting due to the low carbon solubility in Cu, in contrast to the precipitation process observed with Ni [81]. Additionally, other groups investigated alternative metal substrates such as palladium, iridium, and cobalt, refining their methods to produce high-quality graphene with various precursors and deposition temperatures [82–85]. These efforts broadened the range of materials and conditions suitable for large-area graphene production.

However, despite these advancements, challenges remain in scaling up the CVD process. Issues such as high manufacturing costs, the need for graphene transfer or substrate removal, and optimizing synthesis conditions for large-scale production must still be addressed [86].

Other methods

Other methods for graphene synthesis include thermal pyrolysis [87–91], laser-assisted techniques [92–96], gas phase synthesis [97], flash joule heating of carbon sources [98], epitaxial growth [30,99–101], electrochemical exfoliation [102,103], liquid phase exfoliation [104–106], unzipping carbon nanotubes [107,108] and others [109–112]. Each method presents its own set of advantages and challenges, contributing to a diverse array of production techniques. These approaches differ in factors such as complexity, cost-effectiveness, and the level of control over the final graphene properties. As such, selecting the most suitable method depends on the specific demands of the application and the required material characteristics.

1.2.3 Derivatives of graphene

Following the exfoliation of graphite in 2004, a lot of experimental research has largely focused on developing synthetic routes for the efficient production of well-defined graphene sheets. Owing to its exceptional properties, graphene has demonstrated immense potential across a wide range of applications, including touch screens, capacitors, spintronic devices, fuel cells, batteries, sensors, transparent conductive films, high-frequency circuits, environmental remediation, and flexible electronics [25,29,113]. Despite these advantages, pristine graphene exhibits intrinsic limitations that restrict its broader technological deployment.

High-quality graphene is typically produced via micromechanical exfoliation or CVD on metal substrates. While micromechanical exfoliation yields graphene with outstanding crystallinity and electronic performance, it is inherently non-scalable and produces small, randomly distributed flakes unsuitable for large-scale applications [29]. CVD, although capable of producing large-area graphene films, requires high processing temperatures, metal catalysts (such as Cu or Ni), and post-growth transfer

steps that often introduce defects, wrinkles, grain boundaries, and polymer residues. These challenges make the production of large quantities of defect-free graphene technologically complex, costly, and difficult to reproduce [114–116].

As a result, pristine graphene is poorly suited for applications demanding kilogram-scale production, solution-based processing, or thick and porous electrode architectures. Strong π – π stacking and van der Waals interactions between graphene sheets lead to agglomeration and restacking, rendering graphene essentially insoluble in water and most organic solvents [117]. Stable dispersions are therefore difficult to achieve without surfactants or polymer stabilizers, which severely limits film formation, coating, printing, and composite fabrication. This poor processability contrasts sharply with the requirements of modern scalable manufacturing, particularly in energy storage and flexible electronics.

From a chemical perspective, pristine graphene consists entirely of sp^2 -hybridized carbon atoms arranged in an ideal honeycomb lattice. Although this structure underpins graphene's remarkable electronic properties, it also makes graphene chemically inert under most conditions [113]. The absence of surface functional groups hinders chemical functionalization, limits the anchoring of catalytically active species, and weakens interfacial interactions with polymers, oxides, and metals. Consequently, for applications where surface reactivity and chemical tunability are critical such as electrochemical energy storage and catalysis, pristine graphene is often less suitable.

Furthermore, graphene is a zero-band-gap semimetal, which restricts its use in applications requiring a finite band gap, including logic electronics, high-sensitivity sensors, and redox-active electrochemical systems [118]. Although strategies such as nanostructuring, chemical functionalization, doping, or substrate engineering can induce band-gap opening, these modifications frequently compromise graphene's intrinsic carrier mobility and structural integrity. Thus, to overcome these intrinsic limitations of pristine graphene, oxidized and chemically modified graphene derivatives have emerged as practical alternatives [119,120]. The primary objective of graphene derivatisation is to deliberately tailor its physical and chemical properties to

meet the requirements of specific applications. Through chemical modification, key physical characteristic such as electrical resistivity, optical transmittance, electronic band structure, and magnetic behavior can be precisely tuned [120]. Equally important, controlled modification of surface chemistry enables strong interactions with biomolecules, ions, and target analytes, making graphene derivatives highly attractive for applications such as in biosensing, energy storage and environmental remediation [119]. As a result, the scope of applications for graphene derivatives continues to expand rapidly, positioning this class of materials as one of the most versatile platforms in modern materials science [25]. The subsequent section presents a detailed discussion of two widely investigated graphene derivatives, graphene oxide (GO) and reduced graphene oxide (rGO).

Graphene oxide

Graphene oxide (GO) is a chemically modified form of graphene that has a similar hexagonal carbon framework of pristine graphene while being functionalized with various oxygen-containing groups such as hydroxyl ($-\text{OH}$), epoxy ($\text{C}-\text{O}-\text{C}$), carbonyl ($\text{C}=\text{O}$), and carboxylic acid ($-\text{COOH}$). According to the widely accepted Lerf–Klinowski structural model, hydroxyl and epoxy groups are predominantly located on the basal planes of the graphene sheets, whereas carbonyl and carboxyl groups are mainly situated at the sheet edges and defect sites [114,121]. Nevertheless, it should be noted that the precise chemical structure and degree of heterogeneity of GO remain subjects of ongoing debate. Graphene oxide is most commonly synthesized through the chemical oxidation of graphite, a layered material composed of stacked graphene sheets held together by strong $\pi-\pi$ interactions and van der Waals forces. Several classical oxidation methods have been reported in the literature, including those developed by Brodie, Staudenmaier, Hofmann, and Hummers, as well as improved variants such as the method proposed by Tour and co-workers [64,122–124]. These methods typically employ strongly acidic media in combination with powerful oxidizing agents, such as potassium chlorate (KClO_3) or potassium permanganate (KMnO_4). In pristine graphite, the interlayer spacing is approximately 0.335 nm, reflecting the close packing of sp^2 -hybridized carbon layers. During oxidation,

oxygen-containing functional groups are introduced both within the basal planes and along the edges of the graphene sheets. The basal planes are primarily functionalized with epoxy and hydroxyl groups, while carbonyl and carboxyl groups are generated at the edges and defect sites. The incorporation of these oxygen functionalities disrupts the extended sp^2 carbon network and introduces sp^3 -hybridized carbon centers, thereby weakening the interlayer van der Waals interactions that stabilize the graphite structure.

Simultaneously, the polar oxygen-containing groups exhibit strong affinity toward water molecules, leading to the intercalation of water between adjacent layers. As a combined effect of functional group insertion and solvent intercalation, the interlayer spacing expands significantly, typically reaching 0.6–1.0 nm or even higher under hydrated conditions. This expansion facilitates further penetration of oxidizing species and ultimately enables the exfoliation of graphite oxide into single- or few-layer graphene oxide sheets through sonication or mechanical agitation. This structural transformation from graphite to graphene oxide is clearly evidenced in X-ray diffraction (XRD) patterns, where the sharp (002) reflection of graphite at approximately 26° disappears and a new diffraction peak emerges at around $10\text{--}12^\circ$, corresponding to the increased interlayer spacing of GO as shown in Figure 1.5. The enlarged interlayer distance represents a defining structural feature that distinguishes GO from pristine graphite.

The presence of surface oxygen functionalities also imparts significant chemical reactivity, enabling further chemical modification. However, exfoliated GO often exhibits a tendency to aggregate in water and polar organic solvents such as ethylene glycol, DMF, NMP, and THF due to π – π stacking interactions, leading to the formation of larger GO aggregates [119]. To mitigate this issue, various stabilizing agents, including octadecylamine, ionic liquids, and even DNA have been employed to enhance dispersion stability [119]. Further, due to its rich surface chemistry, GO serves as a versatile precursor for the synthesis of graphene derivatives via covalent functionalization. For instance, one of the earliest reports of GO functionalization was presented by Stankovich et al. [125] in 2006, in which GO was chemically modified

using organic isocyanates, enabling the exfoliation of individual GO sheets and their dispersion within polymer matrices.

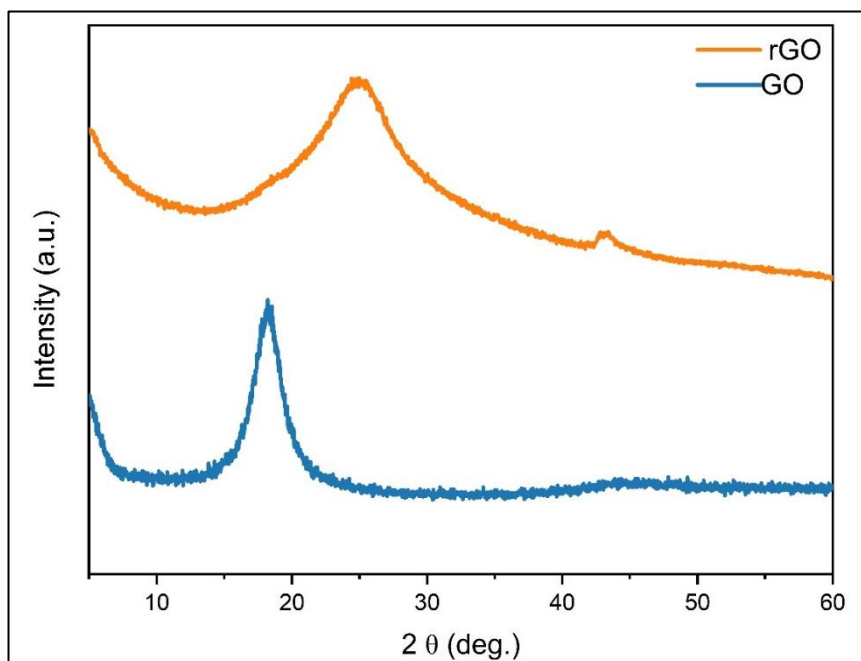


Figure 1.5. XRD patterns of GO and rGO.

Reduced Graphene Oxide (rGO)

In efforts to obtain graphene-based materials with properties approaching those of pristine graphene, extensive research has focused on the removal of oxygen-containing functional groups from graphene oxide (GO). In principle, reductive treatment of GO should eliminate these oxygen functionalities and restore the sp^2 -hybridized carbon network by converting sp^3 -hybridized carbon atoms back to sp^2 , yielding an aromatic and defect-free graphene lattice. However, experimental studies consistently show that even after reduction, a substantial fraction of oxygen groups and structural defects remains. While GO contains a high density of oxygen-containing functional groups and expanded interlayer spacing, reduction removes a significant fraction of these functionalities, leading to substantial structural and electronic changes.

During the reduction process, oxygen-containing groups such as epoxy, hydroxyl, carbonyl, and carboxyl moieties are eliminated from both the basal plane and sheet edges in the form of CO, CO₂, or H₂O, depending on the reduction route. As the oxygen content decreases, the large interlayer spacing in GO is significantly reduced. Consequently, the interlayer distance contracts from values typically in the range of 0.6–1.0 nm in GO to approximately 0.34–0.40 nm in rGO, approaching but not fully reaching that of pristine graphite. This incomplete restoration reflects the presence of residual oxygen groups, structural defects, and vacancies generated during oxidation and reduction. These structural changes are clearly evident in X-ray diffraction (XRD) patterns. The characteristic GO peak at $\sim 10\text{--}12^\circ$ disappears after reduction, while a broad diffraction peak emerges around $24\text{--}26^\circ$, indicating reduced interlayer spacing as shown in Figure 1.5. Raman spectroscopy further confirms the defect-rich nature of rGO, typically showing an increased D/G intensity ratio due to defect generation. Such defects strongly influence the properties of rGO, most notably its electrical conductivity. Consequently, graphene obtained via GO reduction is commonly referred to using specific terminology, such as chemically converted graphene, chemically reduced graphene, rGO, or thermally reduced graphene to distinguish it from pristine graphene.

A wide range of GO reduction strategies has been explored, including thermal annealing, chemical reduction, electrochemical methods, and even biological approaches. Despite these extensive efforts, complete conversion of GO into pristine graphene has not yet been achieved. Residual epoxy and hydroxyl groups are invariably present on the basal plane of rGO. This is also supported by DFT studies which confirm that the total removal of oxygen-containing functional groups through chemical or thermal reduction is thermodynamically and kinetically unfavorable. In particular, modeling of graphite oxide (graphene oxide) by Boukhvalov and Katsnelson [126] showed that configurations containing hydroxyl and epoxy groups correspond to global energy minima. As a result, these oxygen functionalities are thermodynamically stable, making their complete removal and hence full restoration to pristine graphene, intrinsically difficult [119].

1.3 Graphene for electrochemical energy storage

1.3.1 Evolution of supercapacitors

The earliest form of energy storage involving separated electric charge was the Leyden jar, invented in 1745–1746 by Ewald Georg von Kleist and shortly afterward by Pieter van Musschenbroek [127]. It comprised of a glass container with metal foil-coated surfaces and acidic electrolytes. This device is recognized as the first practical capacitor and laid the conceptual foundation for later, more advanced charge-storage systems. Although it functioned as a purely electrostatic capacitor, the underlying charge-storage mechanism of the Leyden jar remained poorly understood for nearly 140 years, largely due to the absence of knowledge regarding subatomic particles, particularly electrons [127].

Significant progress in understanding interfacial charge storage emerged in the nineteenth century with advances in electrochemistry and atomic theory. A major milestone was achieved when Hermann von Helmholtz first described the concept of the electrochemical double layer (EDL) at the electrode–electrolyte interface in 1853 [128]. Helmholtz proposed that charge separation occurs through the formation of two oppositely charged layers at the interface, providing the first theoretical explanation for capacitive charge storage in electrochemical systems [129].

Between 1910 and 1954, the Helmholtz model was progressively refined through the contributions of several researchers, leading to the modern EDL framework [127]. This comprehensive description accounts for the presence of three distinct regions: (i) the inner Helmholtz layer, consisting of specifically adsorbed ions at the electrode surface; (ii) the outer Helmholtz layer, composed of solvated ions near the electrode; and (iii) the diffuse layer, where ions are distributed according to electrostatic interactions and thermal motion. This refined understanding established the fundamental scientific basis for electrochemical capacitive behavior [129].

Despite these theoretical developments, the practical realization of electrochemical capacitors was not achieved until the mid-twentieth century. In 1957, Howard Becker of General Electric patented an electrochemical capacitor employing porous carbon electrodes immersed in an H_2SO_4 electrolyte [130]. By exploiting the exceptionally

high surface area of porous carbon materials, this device enabled substantially enhanced performance and is widely regarded as the first practical precursor to modern supercapacitors.

Further advancements during the 1960s and 1970s, particularly through industrial research efforts at organizations such as Standard Oil of Ohio (SOHIO), improved electrode fabrication and device design. These developments eventually led to the commercial introduction of electrochemical capacitors, notably by NEC in the late 1970s for applications such as memory backup systems [127,130]. During this period, the term “supercapacitor” became established to distinguish these high-capacitance devices from conventional dielectric capacitors.

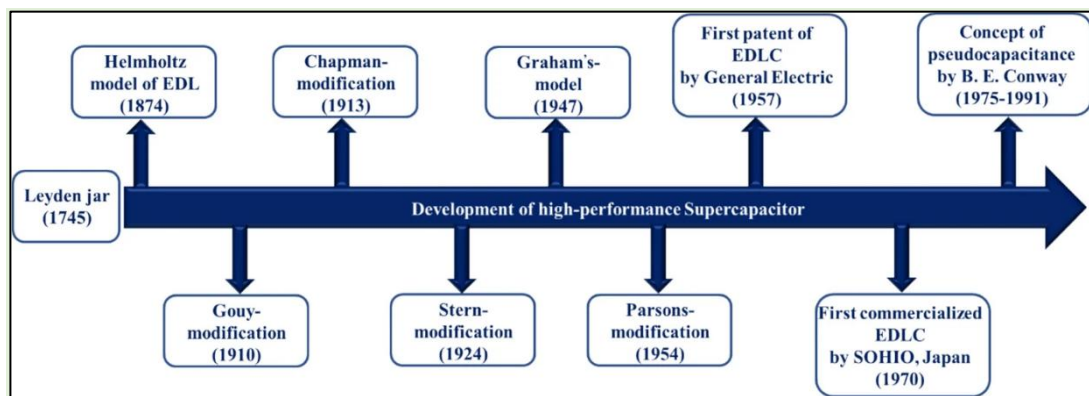


Figure 1.6. Evolution and advancement of supercapacitor technology. Reproduced with permission from Ref. [131].

Around the same period, fundamental research clarified the mechanisms of charge storage in these devices. Between the mid-1970s and the 1990s, Brian Evans Conway conducted extensive studies on ruthenium-oxide systems and formalized the distinction between electric double-layer capacitance and pseudocapacitance [132]. His work established that supercapacitors could rely on a combination of non-Faradaic and Faradaic mechanisms, expanding the range of electrode materials and device configurations. Commercial growth of supercapacitors accelerated in the 1980s and 1990s with improved electrode materials, electrolytes, and cell designs. Companies such as Panasonic, ELNA, and Maxwell Technologies contributed to broader market adoption by producing cells with lower internal resistance and higher performance.

During this period, materials science played a decisive role in advancing supercapacitor technology [130]. Activated carbons became the dominant electrode material for EDLCs due to their high surface area, chemical stability, and low cost. However, limitations associated with pore accessibility, electrical conductivity, and ion transport motivated the exploration of advanced carbon nanostructures. This led to the development of carbon aerogels, carbon nanotubes, and, more recently, two-dimensional carbon materials [133].

The isolation of graphene marked a transformative milestone in supercapacitor research. Owing to its atomically thin structure, exceptionally high specific surface area, excellent electrical conductivity, and mechanical robustness, graphene offers distinct advantages over conventional carbon materials for electrochemical energy storage. These properties enable efficient charge transport, enhanced electrolyte accessibility, and improved utilization of active surface area. As a result, graphene and its derivatives have emerged as highly promising electrode materials for next-generation supercapacitors [133]. A brief overview of the evolution of supercapacitor technology is illustrated in Figure 1.6.

1.4 Classification of supercapacitors

1.4.1 Classification based on charge storage mechanism

Supercapacitors can be classified into three main categories depending on the energy storage mechanism: (1) Electric double layer capacitor (EDLC) (2) pseudocapacitors and 3) hybrid supercapacitors (Figure 1.7). In this section we will discuss those three.

Electric double layer capacitor

In electric double-layer capacitors, energy is stored through a purely electrostatic process that occurs at the boundary between the electrode and the electrolyte (Figure 1.8 (a)). Rather than involving chemical reactions, the mechanism relies on the physical separation of charges at this interface. When a voltage is applied, charges accumulate on the surface of the electrode, and oppositely charged ions from the electrolyte migrate toward it. Due to electrostatic attraction and intermolecular

interactions, these ions arrange themselves in an ordered manner near the electrode surface, creating two closely spaced layers of opposite charge [134].

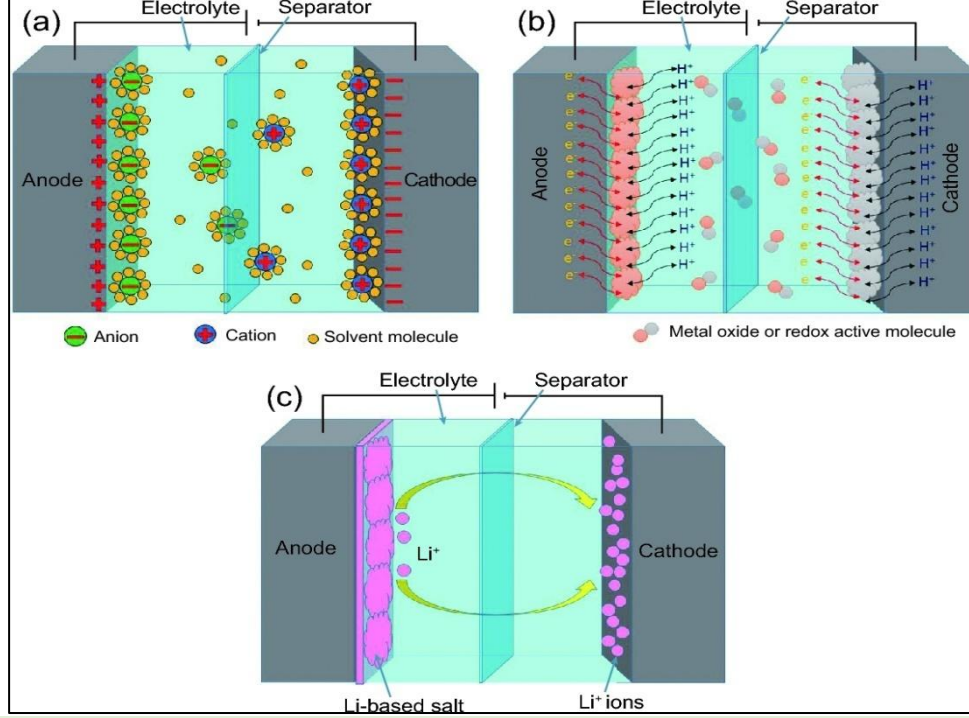


Figure 1.7. Schematic illustration of (a) electrical double-layer capacitor (b) pseudocapacitor, and (c) hybrid supercapacitor. Reproduced with permission from Ref. [135].

This interfacial arrangement of oppositely charged species gives rise to what Hermann von Helmholtz described in 1853 as the electrical double layer capacitance, C [136].

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad (1.2)$$

Where, ϵ_r dielectric constant of the electrolyte, ϵ_0 denotes the permittivity of free space, d corresponds to the thickness of the electrical double layer, and A is the accessible surface area of the electrode. Later, the classical Helmholtz model of the electric double layer was extended by Gouy and Chapman [138,139] by incorporating the effect of thermal motion of electrolyte ions. They proposed that ions are not rigidly fixed at the electrode surface but are continuously distributed within the electrolyte due to thermal agitation, giving rise to a diffuse electric double layer (Figure 1.8 (b)). Consequently, the electrostatic potential decreases gradually from the electrode surface into the bulk solution rather than exhibiting an abrupt drop.

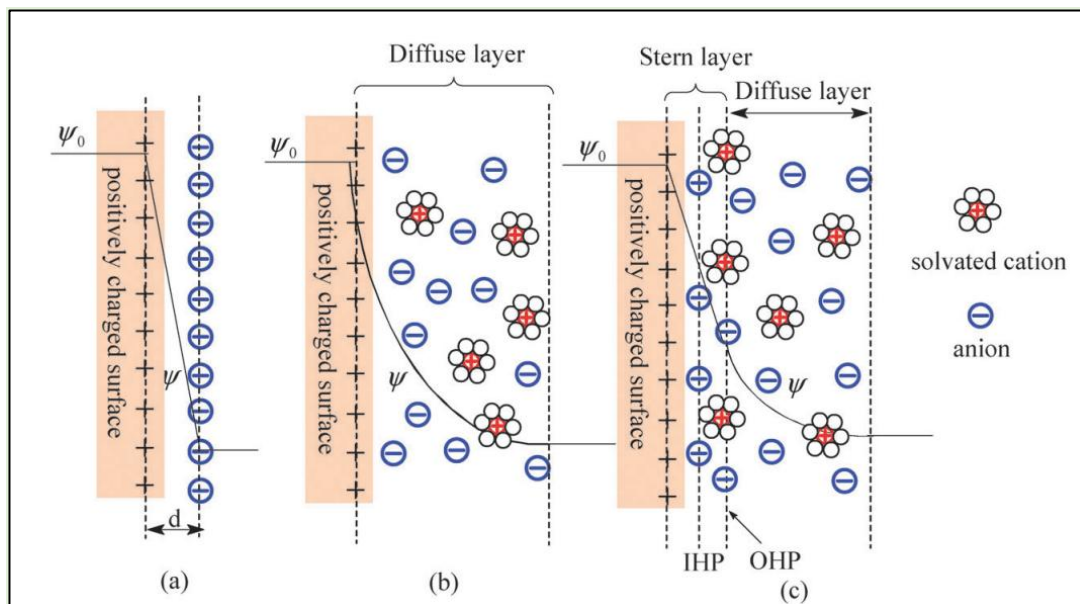


Figure 1.8. Schematic representations of the electrical double layer formed at a positively charged surface: (a) the Helmholtz model, (b) the Gouy–Chapman model, and (c) the Stern model, highlighting the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP). Reproduced with permission from Ref. [137].

Despite this improvement, the Gouy–Chapman model assumes point-like ions and neglects finite ion size, solvation, and specific adsorption effects. These assumptions lead to an overestimation of the electric double-layer capacitance. To address these limitations, Stern proposed a modified model in 1924 [140], which combines the Helmholtz and Gouy–Chapman concepts. In the Stern model, the electric double layer is divided into two distinct regions: a compact (Stern) layer adjacent to the electrode surface and an outer diffuse layer extending into the bulk electrolyte, as illustrated in Figure 1.8 (c). The compact (Stern) layer consists of ions located close to the electrode surface. Some ions are specifically adsorbed and can interact directly with the electrode, defining the inner Helmholtz plane (IHP). Other ions remain fully solvated and are attracted only by electrostatic forces; their closest approach to the electrode defines the outer Helmholtz plane (OHP). Beyond the compact layer, ions are distributed more freely in the electrolyte, forming the diffuse layer described by the Gouy–Chapman model.

Therefore, the total double-layer capacitance (C_{dl}) can be expressed as the series combination of the compact-layer capacitance (C_H) and diffuse-layer capacitance (C_{diff}), according to:

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \quad (1.3)$$

In general, aqueous acidic or alkaline electrolytes provide higher specific capacitance than non-aqueous systems due to their higher ionic conductivity and smaller ion sizes. However, organic electrolytes and ionic liquids are more widely employed in electric double-layer capacitors (EDLCs) because they allow substantially wider operating potential windows. Organic electrolytes typically support operating voltages of up to 2.5–2.7 V in symmetric devices, while ionic liquids can extend the operating potential window further to approximately 3.5–4.0 V, depending on the ion chemistry and electrode material [136].

Since the energy stored in a capacitor is proportional to the square of the operating voltage, as described by $E = \frac{1}{2} CV^2$, even a moderate increase in voltage leads to a pronounced enhancement in energy density. For instance, a threefold increase in operating voltage results in nearly an order-of-magnitude increase in stored energy at constant capacitance [136].

One key advantage of EDLCs is that they store charge without faradaic reactions, so the electrode structure remains stable. This allows them to operate for millions of charge–discharge cycles, unlike batteries that typically last only a few thousand cycles. In addition, since the electrolyte solvent does not directly take part in the storage process, EDLCs provide more flexibility in electrolyte selection and can deliver high power performance over a broad temperature range, even at temperatures as low as $-40\text{ }^{\circ}\text{C}$ when appropriate organic electrolytes are used [136].

Despite these advantages, EDLCs remain constrained by relatively low energy density, which arises from their purely electrostatic charge storage mechanism. As a result, current research efforts are primarily focused on enhancing the energy density of EDLCs and extending their operational temperature window into regimes where conventional battery technologies cannot function reliably [8].

Pseudocapacitors

The concept of pseudocapacitance was introduced in the early 1960s by B. E. Conway and E. Gileadi, who sought to explain electrochemical charge storage processes that exhibited capacitor-like behavior but originated from Faradaic charge transfer reactions rather than purely electrostatic charge separation [141]. Unlike electric double-layer capacitance (EDLC), pseudocapacitance arises from fast, highly reversible surface or near-surface redox reactions, leading to a nearly linear relationship between stored charge and applied potential. Historically, the term “pseudocapacitance” evolved from earlier work by David C. Grahame, who used the term *pseudocapacity* in 1941 to describe reversible charge not associated with double-layer formation [141]. Conway later formalized the concept by connecting thermodynamics and kinetics of Faradaic reactions to a capacitance-like response.

As summarized in Figure 1.9, the understanding of pseudocapacitance has evolved from early surface adsorption phenomena to encompass redox reactions in metal oxides and, more recently, fast ion-intercalation processes in crystalline hosts [142]. Conway classified pseudocapacitance into three fundamental types, illustrated schematically in Figure 1.10: (i) adsorption (including underpotential deposition), (ii) redox pseudocapacitance, and (iii) intercalation pseudocapacitance.

The following section discusses each of these types in detail.

Adsorption pseudocapacitance

Adsorption pseudocapacitance represents the earliest recognized form of pseudocapacitance described by Conway and Gileadi in 1962 [142]. It arises from the electrochemical adsorption of ions or atoms onto an electrode surface, following a Langmuir-type adsorption isotherm. In these systems, charge storage occurs through partial charge transfer during the adsorption of ions or atoms onto the electrode surface. The extent of adsorption varies continuously with potential, leading to a capacitance defined as the derivative of surface coverage with respect to potential.

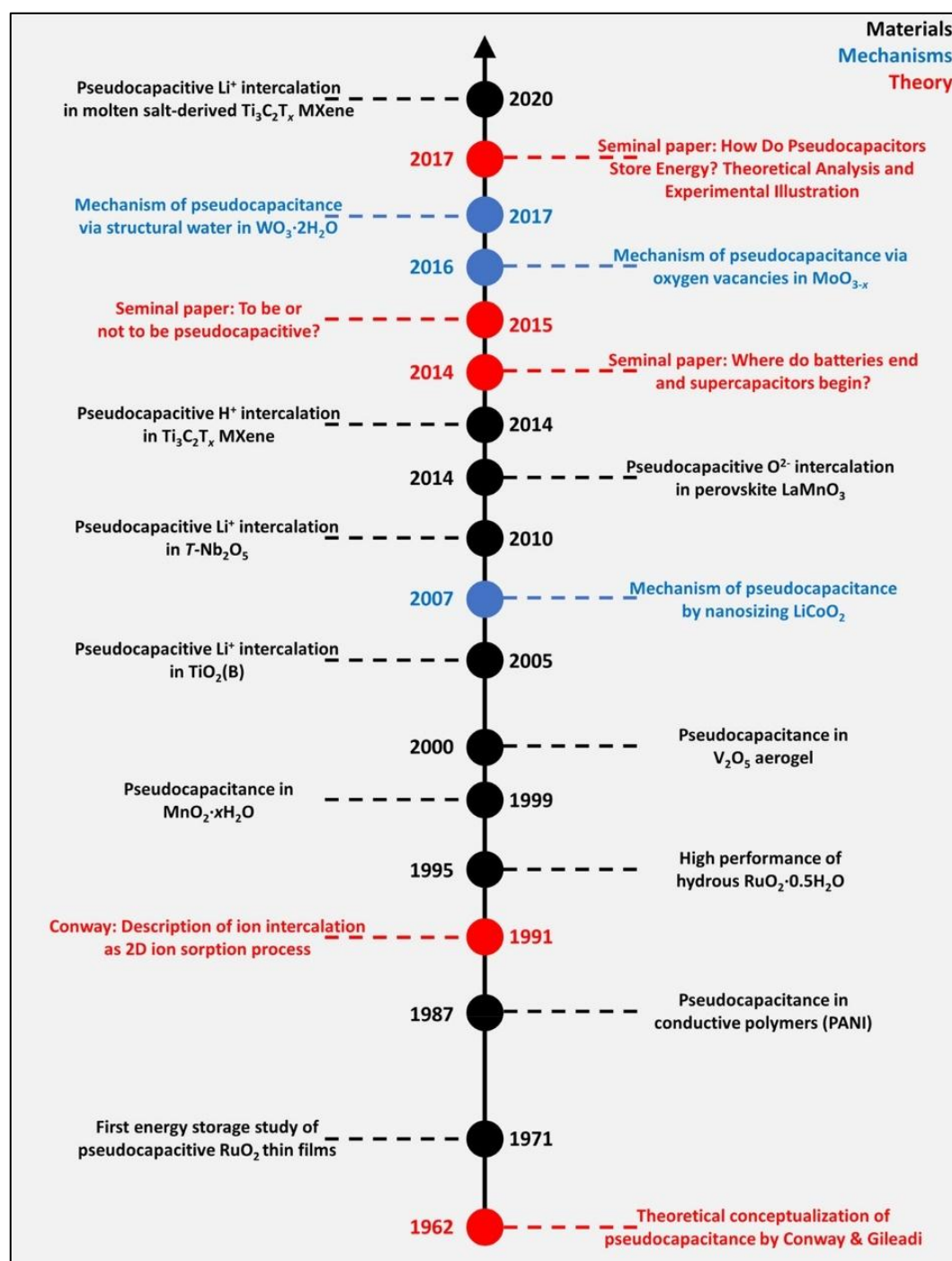


Figure 1.9. Overview of key advances in pseudocapacitance. Reproduced with permission from Ref. [142].

Although the process is Faradaic in nature, it is not diffusion-limited, and the cyclic voltammograms often show a linear dependence of current on scan rate (Figure 1.10 (d)), a hallmark of capacitive behavior [142]. A classic example of adsorption pseudocapacitance is underpotential deposition (UPD), in which a metal monolayer is

deposited onto a foreign metal substrate at potentials more positive than those required for bulk deposition. The adsorption pseudocapacitance is illustrated schematically in Figure 1.10 (a).

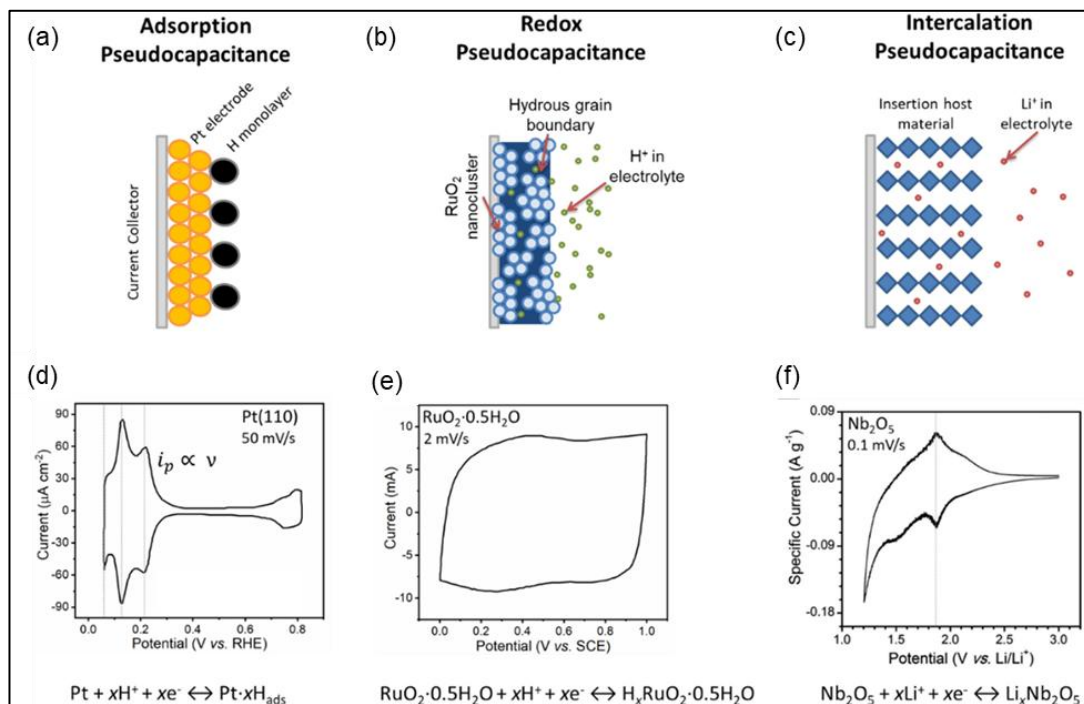


Figure 1.10. (a–c) Schematic depiction of the three fundamental pseudocapacitive charge-storage mechanisms proposed by Conway, with (d–f) the corresponding cyclic voltammetric responses. (a) Adsorption pseudocapacitance, (b) redox pseudocapacitance, and (c) intercalation pseudocapacitance. (d) Cyclic voltammogram of a Pt (110) electrode in 0.1 M HClO₄ aqueous electrolyte recorded at a scan rate of 50 mV s⁻¹. (e) Cyclic voltammogram of a RuO₂·0.5H₂O electrode in 0.5 M H₂SO₄ aqueous electrolyte measured at 2 mV s⁻¹. (f) Cyclic voltammogram of a nanocrystalline T-Nb₂O₅ film in a nonaqueous Li⁺ electrolyte obtained at 0.1 mV s⁻¹. Reproduced with permission from [142].

Redox pseudocapacitance

Redox pseudocapacitance gained prominence following the seminal work of Trasatti and Buzzanca (1971) on hydrous ruthenium oxide ($\text{RuO}_2 \cdot n\text{H}_2\text{O}$), which demonstrated capacitor-like electrochemical behavior in acidic electrolytes [143]. Here, charge storage is generally associated with reversible Faradaic redox processes occurring at or near the electrode surface. Unlike battery-type electrodes, these reactions do not involve long-range phase transformations and are not limited by solid-state diffusion. Consequently, the electrochemical response often appears nearly rectangular, closely resembling ideal capacitive behavior [142]. This mechanism is illustrated in Figure 1.10 (b) and 1.10 (e), where hydrous RuO_2 exhibits a highly symmetric and reversible cyclic voltammogram in an acidic electrolyte. Structural water, surface disorder, and nanoscale dimensions play a critical role by facilitating rapid proton or cation transport and minimizing diffusion limitations. As a result, redox pseudocapacitive materials can deliver high specific capacitance while retaining excellent rate capability. Beyond RuO_2 , extensive research has demonstrated redox pseudocapacitance in materials such as MnO_2 , NiO , Co_3O_4 , and conducting polymers (e.g., polyaniline and polypyrrole) [142].

Intercalation pseudocapacitance

Intercalation pseudocapacitance, first introduced by Brian E. Conway in the early 1990s, extends the concept of pseudocapacitance to solid-solution electrochemical intercalation processes [132,144]. It describes ion-insertion reactions that are not governed by slow solid-state diffusion and that proceed without first-order phase transformation. Unlike conventional battery electrodes, where ion insertion typically induces distinct phase changes, pseudocapacitive intercalation occurs through continuous solid-solution behavior, enabling rapid and highly reversible charge storage with capacitor-like kinetics [142].

This mechanism gained recognition through studies on materials such as monoclinic bronze-structured titanium dioxide and orthorhombic T-phase niobium pentoxide, in which ions can migrate rapidly along specific crystallographic directions, resulting in capacitor-like electrochemical kinetics [144,145]. This intercalation pseudocapacitive

mechanism is schematically illustrated in Figure 1.10 (c), while Figure 1.10 (f) presents the cyclic voltammogram of a T-Nb₂O₅ film measured in a nonaqueous Li⁺ electrolyte at a scan rate of 0.1 mV s⁻¹. The dashed line in Figure 1.10 (f) highlights the high reversibility of the Faradaic intercalation process [142]. Related behavior has also been observed in two-dimensional materials, including MXenes, where fast ion transport and minimal structural changes contribute to pseudocapacitive charge storage [146]. As a result of these characteristics, intercalation pseudocapacitive materials can deliver higher energy density than electrical double-layer capacitors while retaining high power capability. However, electrodes demonstrating pseudocapacitive behavior are susceptible to shrinking and swelling during charge-discharge cycling which results in reduced cycling stability and shorter cycle life.

Hybrid supercapacitors

Hybrid supercapacitors are designed to bridge the performance gap between electric double-layer capacitors and batteries by integrating two electrodes with fundamentally different charge-storage behaviors in a single device [147]. Typically, a battery-type faradaic electrode is coupled with a capacitor-type electrode, enabling the system to deliver higher energy density while retaining the rapid charge-discharge capability characteristic of supercapacitors. Moreover, careful selection of electrode materials can extend the operating voltage window of the device, resulting in further improvement in overall energy density [136].

In a typical hybrid configuration, the faradaic electrode functions as the energy source, whereas the capacitive electrode acts as the power source [148]. A schematic illustration of this concept is shown in Figure 1.7 (c). A wide range of positive and negative electrode combinations has been explored using aqueous and non-aqueous electrolytes. Although the incorporation of a battery-type electrode typically enhances energy density, it often compromises cycling stability; this trade-off represents a major challenge in the development of hybrid supercapacitors [149].

The hybrid supercapacitor concept originated from advances in lithium-ion battery research. An early and influential demonstration was reported in 1999 by Amatucci

and co-workers [150], who combined a nanostructured lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) negative electrode with an activated carbon positive electrode to construct a 2.8 V hybrid device exceeding 10 Wh kg^{-1} in energy density. The lithium titanate electrode provided high rate capability and long cycle life due to its negligible volume change and the absence of solid electrolyte interphase formation [147].

Subsequent research has expanded hybrid supercapacitor systems to include a wide range of metal ions. Devices based on monovalent ions, particularly lithium and sodium, have been extensively investigated; however, their practical deployment is limited by safety concerns related to highly reactive metals and flammable organic electrolytes, as well as increasing material costs driven by resource scarcity [148]. These limitations have motivated growing interest in multivalent-ion-based hybrids, such as those employing magnesium, calcium, aluminum, or zinc ions, which offer advantages in terms of safety, abundance, and cost [148].

With continued progress in nanostructured electrode materials, hybrid supercapacitors are expected to play an important role in applications requiring high power output combined with moderate energy density and medium cycle life, occupying a performance space intermediate between conventional supercapacitors and rechargeable batteries [147–149].

1.4.2 Classification based on electrode configuration

Supercapacitor devices may also be categorized according to the electrode configuration, namely symmetric, asymmetric, and hybrid systems [127,151]. Symmetric supercapacitors consist of two identical electrodes with the same material and mass loading. While this configuration offers excellent reversibility and long-term cycling stability, it is generally constrained by a narrow operating voltage window, which limits the achievable energy density. Carbon-based materials are most commonly used in symmetric devices due to their high surface area, chemical stability, and good electrical conductivity [127].

Asymmetric supercapacitors, in contrast, utilize two electrochemically dissimilar electrodes, typically combining an EDLC-type electrode with a pseudocapacitive

electrode. This configuration enables an expansion of the operating voltage window and consequently enhances the energy density of the device [127]. Hybrid supercapacitors as discussed earlier consists of two electrodes, in which one electrode exhibits battery-like, diffusion-controlled faradaic behavior, while the other electrode operates via capacitive or pseudocapacitive mechanisms. This electrode pairing exploits the complementary strengths of each component, leading to a substantial increase in working voltage and energy density without severely sacrificing power capability. Owing to these attributes, hybrid supercapacitors are particularly attractive for applications requiring sustained power delivery. However, precise charge and mass balancing between the positive and negative electrodes is crucial to ensure optimal performance and long-term stability [127,147–149].

1.5 Performance evaluation

The electrochemical performance of supercapacitors is commonly assessed using parameters such as specific capacitance, energy density, power density, coulombic efficiency and cycling stability [8,13]. These parameters can be obtained from three-electrode (single-electrode) measurements or from two-electrode (full-cell) configurations. Importantly, electrochemical performance derived from full-cell measurements can be normalized either to the total mass of both electrodes or to the mass of a single electrode [152]. Therefore, it is essential to clearly specify the mass normalization when reporting electrochemical performance metrics. In this work, all electrochemical parameters are reported with respect to a single electrode mass.

Specific capacitance

Specific capacitance (C_{SP}) represents the charge storage capability of an electrode material per unit mass and is typically expressed in farads per gram ($F\ g^{-1}$). It is one of the most fundamental parameters used to evaluate supercapacitor electrodes and can be derived from cyclic voltammetry (CV) or galvanostatic charge–discharge (GCD) measurements [13]. Equations 1.4 and 1.5 were utilized to determine C_{SP} ($F\ g^{-1}$) from the CV and GCD data in the three-electrode configuration.[153,154] The capacitance of the graphite sheet was neglected.

$$C_s = \frac{A}{\Delta V \times v \times m} \quad (1.4)$$

$$C_s = \frac{I \times \Delta t}{m \times \Delta V} \quad (1.5)$$

Where, A , ΔV , v , m , Δt and $\frac{I}{m}$ represents the integral area of CV loops, sweep potential window (V), scan rate ($V s^{-1}$), mass of electrodes (g), discharging time (s) and applied current density ($A g^{-1}$), respectively.

Equations 1.6 and 1.7 were utilized to determine the C_{SP} ($F g^{-1}$) from the CV and GCD data for the symmetric supercapacitor [155].

$$C_s = \frac{2A}{\Delta V \times v \times m} \quad (1.6)$$

$$C_s = \frac{2(I \times \Delta t)}{m \times V} \quad (1.7)$$

A factor of 2 is introduced to account for the series capacitance that arises in a symmetric supercapacitor device.

Energy density

Energy density (E_d) describes the amount of energy stored per unit mass and is expressed in watt-hours per kilogram ($Wh kg^{-1}$). For supercapacitor electrodes, energy density is calculated from the specific capacitance using the following relation [8]:

$$E_d = \frac{1}{2 \times 4} \frac{C_{SP} \times V^2}{3.6} \quad (1.8)$$

where C_{SP} is the specific capacitance ($F g^{-1}$) and V is the operating voltage window (V). The factor of 3.6 converts energy from joules to watt-hours.

Power density

Power density (P_d) reflects the rate at which stored energy can be delivered and is a key parameter distinguishing supercapacitors from batteries. It is expressed in watts per kilogram (W kg^{-1}) and is calculated as [13]:

$$P_d = \frac{E_d}{\Delta t} \times 3600 \quad (1.9)$$

where E_d is the energy density (Wh kg^{-1}) and Δt is the discharge time (s). High power density values indicate rapid charge–discharge capability and efficient electron and ion transport within the electrode material.

Coulombic efficiency

Coulombic efficiency (CE) is defined as the ratio of the charge delivered during discharge to the charge stored during the preceding charge process. It quantifies the cycle-to-cycle charge reversibility of an electrochemical system and is highly sensitive to irreversible processes such as parasitic reactions and side reactions at the electrode–electrolyte interface. An ideal electrochemical system free from parasitic reactions exhibits a coulombic efficiency of unity ($\text{CE}=1$). Any measurable deviation from unity reflects the presence of irreversible processes, such as electrolyte decomposition, surface reactions, or self-discharge phenomena [155].

Dahn and co-workers [156] emphasized that coulombic efficiency is extremely sensitive to even very small parasitic reaction rates and therefore serves as a powerful diagnostic metric for predicting long-term electrochemical stability. Their analysis demonstrated that achieving long service lifetimes requires coulombic efficiencies extraordinarily close to unity; for example, a cell intended to operate for approximately ten years under daily cycling would require an average coulombic efficiency on the order of 0.99997.

Coulombic efficiency can thus, be employed to determine the electrochemical stability window of new electrode–electrolyte systems. In this approach, the potential window is gradually expanded step-by-step and the upper or lower potential limit is defined as the point at which coulombic efficiency begins to deviate measurably from unity, indicating the onset of irreversible reactions such as electrolyte decomposition. Coulombic efficiency can be calculated from either galvanostatic charge–discharge (GCD) curves or cyclic voltammetry (CV) measurements. In particular, CV-based coulombic efficiency measurements conducted at low scan rates (typically 5–10 mV s⁻¹) are commonly employed to ascertain the safe operating potential window [157,158].

For galvanostatic charge–discharge measurements, coulombic efficiency is calculated as:

$$CE = \frac{I_{discharge} t_{discharge}}{I_{charge} t_{charge}} \quad (1.10)$$

where I is the applied current and t is the corresponding charge or discharge time.

For cyclic voltammetry measurements, coulombic efficiency is calculated from the integrated anodic and cathodic charges:

$$CE = \frac{\int I_{cathodic} dt}{\int I_{anodic} dt} \quad (1.11)$$

The charge associated with each half-cycle is obtained by numerical integration of the current–time response using potentiostat software or numerical methods.

Cycling stability

Cycling stability is a critical parameter for evaluating the long-term durability and practical applicability of supercapacitor electrodes [8,13]. It reflects the ability of an electrode material to retain its capacitance upon repeated charge–discharge cycling, which is particularly important for high-power and long-life energy storage

applications. Cycling stability is commonly assessed by performing repeated galvanostatic charge–discharge (GCD) cycles or continuous cyclic voltammetry (CV) cycling over several thousand cycles at a fixed current density or scan rate. The capacitance retention after cycling is calculated as:

$$\text{Capacitance retention (\%)} = \frac{C_n}{C_0} \quad (1.12)$$

Where, C_0 is the initial specific capacitance, and C_n is the specific capacitance after n charge–discharge cycles. A high capacitance retention (typically >80–90% after several thousand cycles) indicates excellent electrochemical stability and structural robustness of the electrode material.

1.6 Reported performance of supercapacitor electrode materials

Following the evaluation criteria discussed above, numerous studies have reported the electrochemical performance of various electrode materials for supercapacitor applications. These materials include activated carbons, transition metal oxides, graphene, and their hybrid composites. While significant improvements have been achieved, practical energy density remains constrained by limitations in operating voltage window, electrode stability, and ion transport kinetics. A comparative overview of representative literature reports is presented in Table 1.2.

Table 1.2: Reported Electrochemical Performance of Representative Supercapacitor Devices.

Materials	Electrolyte	Voltage window (V)	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)	Ref.
Activated carbon	BMPY-TFSI	3	25	100	[159]
ReS ₂	TEABF ₄	2	28.5	500	[160]

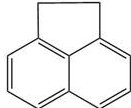
Porous graphene macroform	1 M TEABF ₄ /ACN	2.5	23.5	63	[161]
MoS ₂ nanosheets	0.5 M TEABF ₄	3	20.68	--	[162]
Graphene/V ₂ O ₅	LiClO ₄ /PC	2.5	80.4	275	[163]
MoSe ₂ nanosheets	0.5 M TEABF ₄	3	20.31	1125	[164]
Porous carbon	EMIMBF ₄	2	20	3100	[165]
Siloxene	0.5 M TEABF ₄	3	5.08	375	[166]
Poly(ionic liquid)-modified rGO	[MPPy] [TFSI]	2	40	2100	[167]
Blue TiO ₂ Sheets	1M TEABF ₄	3	6	750	[168]
BDA/rGO	1M TEABF ₄ /ACN	2.5	34	425	[169]
Defective boron nanosheet	BMIMBF ₄	3	25.1	636.1	[170]
Tris-rGO	TEABF ₄	3.5	51	552	[171]
Silicon oxycarbide	TEABF ₄	3	20.89	750	[172]
Graphene-CMK-5	EMIMBF ₄	3.5	60.7	174	[173]
Reduced graphene oxide	BMIPF ₆	4	18.9	2800	[174]
Reduced graphene oxide	[SET ₃][TFSI]	2.5	17.7	875	[175]
Hydrothermally prepared rGO	TEABF ₄	3	35.58	7500	[176]
Sonochemically prepared rGO	TEABF ₄	3	38.07	1500	[177]
Graphene	TEABF ₄	3	44.95	750	[178]

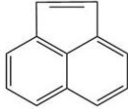
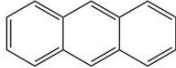
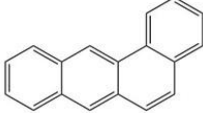
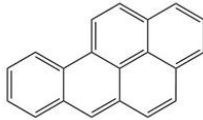
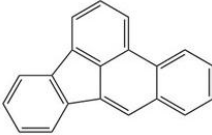
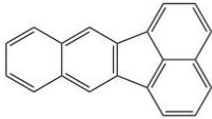
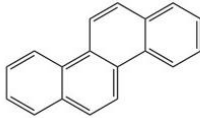
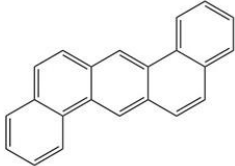
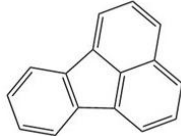
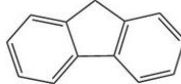
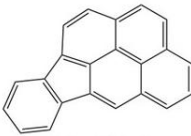
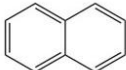
1.7 Graphene for environmental remediation

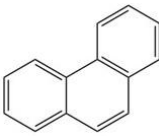
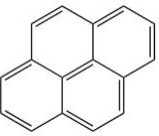
1.7.1 Polycyclic aromatic hydrocarbons

Among the diverse classes of chemical pollutants affecting water bodies, polycyclic aromatic hydrocarbons (PAHs) have gained considerable scientific and regulatory attention due to their environmental stability, resistance to degradation, and potential for bioaccumulation. PAHs are a class of organic compounds composed of two or more fused aromatic rings. They are primarily generated through the incomplete combustion of organic materials such as coal, petroleum, biomass, and fossil fuels, and are released into the environment via both natural sources (e.g., forest fires and volcanic activity) and anthropogenic sources including vehicular emissions, industrial processes and oil spills [179–182]. Once released, PAHs are readily transported through the atmosphere and subsequently deposited onto land and water surfaces, making aquatic ecosystems important sinks for these contaminants. The environmental and health implications of PAH contamination are of significant concern. Humans are exposed to PAHs mainly through contaminated food consumption, inhalation of polluted air, and direct contact with affected surfaces. Short-term exposure may result in gastrointestinal disturbances and dermatological symptoms, including nausea, reduced appetite, itching, and diarrhea. Importantly, several PAH constituents are recognized as carcinogenic by the International Agency for Research on Cancer, and sustained exposure has been associated with elevated risks of multiple malignancies, such as cancers of the lung, stomach, skin, esophagus, prostate, kidney, and the male reproductive system. As a result, the United States Environmental Protection Agency (US EPA) has identified 16 such PAHs (Table 1.3) as emerging pollutants [183]. An overview of the adverse health effects and complications associated with human exposure to PAHs is presented in Figure 1.12.

Table 1.3: List of priority PAHs as identified by USEPA.

Sl. No.	PAHs	Structure
1	Acenaphthene	

2	Acenaphthylene	
3	Anthracene	
4	Benzo[a]anthracene	
5	Benzo[a]pyrene	
6	Benzo[b]fluoranthene	
7	Benzo[g,h,i]perylene	
8	Benzo[k]fluoranthene	
9	Chrysene	
10	Dibenzo[a,h]anthracene	
11	Fluoranthene	
12	Fluorene	
13	Indeno[1,2,3-cd]pyrene	
14	Naphthalene	

15	Phenanthrene	
16	Pyrene	

1.7.2 The adsorption process

Adsorption refers to the accumulation of molecules from a surrounding gas or liquid phase onto the surface of a solid material. This phenomenon arises due to attractive forces between the surface of the solid and the molecules present in the fluid phase, which create a region of lower potential energy near the surface. As a result, molecules tend to concentrate at the solid–fluid interface rather than remaining uniformly distributed in the bulk phase [184].

The solid material that provides the surface for interaction is termed the adsorbent, while the species that becomes attached to this surface is known as the adsorbate. When an adsorbent comes into contact with a fluid containing the target adsorbate, the molecules migrate from the bulk phase toward the solid–fluid interface and occupy available surface sites and pores. This process proceeds until an equilibrium is established between the adsorbed molecules and those remaining in the fluid phase. Following adsorption, the adsorbent loaded with the adsorbate can be separated from the treated medium, commonly by filtration, resulting in pollutant removal. In many cases, the adsorbent can be regenerated through desorption and reused, enhancing the economic and environmental feasibility of the process [18,185,186].

The efficiency and mechanism of adsorption are governed by several factors, including the physicochemical properties of both the adsorbent and adsorbate, as well as the operating conditions. Parameters such as surface area, pore size distribution, particle size, and surface functional groups of the adsorbent strongly influence adsorption capacity. In aqueous systems, solution conditions such as pH, temperature,

contact time, adsorbent dosage, and the presence of interfering ions further affect adsorption behavior [185,186].

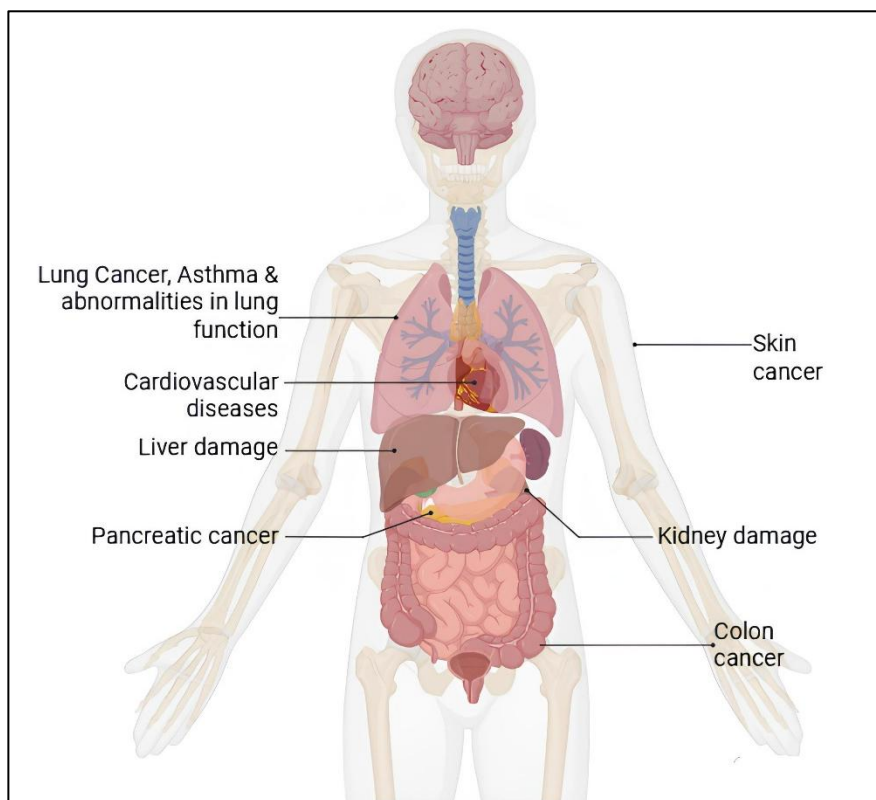


Figure 1.11. Adverse health effects of PAH exposure on the human body.

Depending on the nature of the interactions between the adsorbent and adsorbate, adsorption can be broadly classified into physisorption and chemisorption [18,184]. Physisorption occurs through relatively weak intermolecular forces such as van der Waals interactions and electrostatic attraction. During physical adsorption, the electronic structures of both the adsorbent and adsorbate remain largely unchanged, and no new chemical bonds are formed. As a result, physisorption is generally characterized by rapid adsorption–desorption kinetics and a high degree of reversibility, since only a modest energy input is required to overcome these weak interactions.

In contrast, chemisorption involves the formation of stronger chemical bonds between the adsorbate and the surface of the adsorbent through electron sharing or transfer [185,186]. This process alters the electronic structure of the interacting species and is

often associated with higher adsorption energies. Chemisorption is typically more specific and may be less reversible than physisorption, depending on the strength of the chemical bonds formed.

To quantitatively describe adsorption behavior, experimental data are commonly analyzed using adsorption isotherm models and kinetic models [185]. Isotherm models provide insight into adsorption capacity and surface characteristics at equilibrium, kinetic models describe the rate and controlling mechanisms of adsorption. Together, these models form the foundation for understanding and comparing adsorption performance across different adsorbent systems.

1.7.3 Adsorption isotherm models

Adsorption isotherm models describe the equilibrium relationship between the amount of adsorbate retained on an adsorbent surface and its concentration in the aqueous phase at a constant temperature. These models are widely used to interpret adsorption behavior and to evaluate the interaction between adsorbents and adsorbates. By fitting isotherm models to experimental data, insights can be obtained into the adsorption mechanism, including whether adsorption occurs as a monolayer or multilayer process and whether the adsorbent surface exhibits homogeneous or heterogeneous characteristics. Among the various isotherm models proposed, the Langmuir, Freundlich, and Temkin models are most commonly applied to describe the adsorption of organic pollutants in water systems [187–189].

Langmuir isotherm model

The Langmuir adsorption isotherm model is widely used to describe adsorption equilibrium and is based on several fundamental assumptions [187]. The model assumes that adsorption occurs as a monolayer on the surface of the adsorbent, such that each adsorption site can accommodate only one adsorbate molecule. It further assumes that the adsorbent surface is homogeneous, with adsorption sites that are energetically equivalent and equally accessible. In addition, the Langmuir model presumes that the adsorption energy remains constant throughout the adsorption process, indicating uniform adsorbate–surface interactions. Finally, it assumes that

interactions between adsorbed molecules are negligible, such that the adsorption of one molecule does not influence the adsorption behavior of neighboring molecules.

Based on these assumptions, the non-linear form of the Langmuir isotherm is expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1.13)$$

Where, q_e (mg g⁻¹) is the equilibrium adsorption capacity, C_e (mg L⁻¹) is the equilibrium concentration of the adsorbate, q_m (mg g⁻¹) denotes the maximum monolayer adsorption capacity of the adsorbent, K_L is the Langmuir adsorption constant related to the adsorption energy.

In addition, the dimensionless separation factor (R_L), also known as the equilibrium parameter, is widely used to evaluate the favorability of the adsorption process. The separation factor is defined as:

$$R_L = \frac{1}{1 + K_L C_i} \quad (1.14)$$

Where, C_i is the initial concentration of NAP.

The value of R_L , provides qualitative insight into the nature of the adsorption process. Values between 0 and 1 indicate favorable adsorption, $R_L = 1$ corresponds to linear adsorption, $R_L > 1$ denotes unfavorable adsorption, and $R_L = 0$ represents irreversible adsorption.

Further, a distinctive feature of the Langmuir model is its ability to estimate the maximum adsorption capacity, which provides a quantitative measure for comparing the performance of different adsorbents. A good agreement between experimental data and the Langmuir model suggests that adsorption proceeds predominantly via monolayer coverage on a relatively uniform surface.

Freundlich isotherm model

The Freundlich adsorption isotherm model is commonly used to describe adsorption processes occurring on heterogeneous surfaces [189]. Unlike the Langmuir model, the Freundlich isotherm does not assume monolayer adsorption and allows for the

possibility of multilayer adsorption, reflecting variations in adsorption energy across the adsorbent surface. Further, it does not predict a saturation limit but instead suggests that adsorption can occur in multiple layers. The Freundlich isotherm is expressed in its non-linear form as:

$$q_e = K_F C_e^{1/n} \quad (1.15)$$

Where, K_L ($\text{mg g}^{-1} (\text{mg L}^{-1})^n$) is the Freundlich constant indicative of adsorption capacity, n is a dimensionless parameter that indicates adsorption intensity and surface heterogeneity. The magnitude of the parameter n provides insight into the favorability of the adsorption process, with values of $n > 1$, indicating favorable adsorption conditions.

Temkin isotherm model

The Temkin isotherm was proposed to account for the effect of adsorbent–adsorbate interactions on adsorption energetics [188]. Unlike the Langmuir model (which assumes constant adsorption energy) or the Freundlich model (empirical description of heterogeneity), the Temkin approach assumes that the heat of adsorption decreases approximately linearly with increasing surface coverage due to adsorbate–surface interactions and, at higher surface coverage, adsorbate–adsorbate interactions. This makes the Temkin model particularly useful for adsorption systems in which adsorbate–surface interaction energies vary with surface coverage, but the system does not strictly conform to ideal monolayer adsorption or strongly heterogeneous surface behavior. The model is expressed as:

$$q_e = B \ln(K_T C_e) \quad (1.16)$$

Where, K_T (L mg^{-1}) is the Temkin equilibrium binding constant, $B (= \frac{RT}{b})$ is a constant related to the heat of adsorption, with R being the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is temperature (K).

1.7.4 Kinetic models

While adsorption isotherms explain how much of a pollutant can be adsorbed at equilibrium, they do not provide information about how fast the adsorption process occurs. In practical applications, the rate of adsorption and the time required to reach

equilibrium are equally important. This behavior is described using adsorption kinetics, which examines the change in adsorption with time and helps identify the processes controlling adsorption. Among the various kinetic models available, the pseudo-first-order and pseudo-second-order models are most commonly applied to describe adsorption kinetics in aqueous systems [190,191].

Pseudo-first-order (PFO) model

The pseudo-first-order kinetic model was first introduced by Lagergren (1898) to describe liquid–solid adsorption systems based on adsorption capacity rather than solute concentration [190]. The model assumes that the rate of adsorption is proportional to the difference between the equilibrium adsorption capacity and the amount adsorbed at any given time.

It is expressed as:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1.17)$$

where q_e and q_t are the amount of adsorbate adsorbed on adsorbent in $mg\ g^{-1}$ at equilibrium and at any time t (min), respectively, and k_1 is the rate constant of the first-order model (min^{-1}).

The PFO model is commonly used to describe adsorption systems where the adsorption rate decreases exponentially with time and is particularly effective for representing the initial stages of adsorption.

Pseudo-second-order (PSO) model

The pseudo-second-order kinetic model describes adsorption kinetics based on the assumption that the rate of adsorption is proportional to the square of the difference between the equilibrium adsorption capacity and the amount adsorbed at any given time [191]. It is expressed as:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (1.18)$$

where k_2 is the rate constant of the second-order model ($g\ mg^{-1}\ min^{-1}$).

1.4 Adsorption performance of different materials for PAH removal

Significant research efforts have been directed toward the development of effective adsorbent materials for the removal of NAP from aqueous systems. To provide a concise and comparative understanding of these adsorbents, Table 1.4 summarizes key literature reports, highlighting the adsorbent type, isotherm models, maximum adsorption capacity, equilibrium time and percentage removal.

Table 1.4: Reported Adsorbents for PAH Removal.

Adsorbent	Type of PAH	Isotherm model	Maximum adsorption capacity	Equilibrium time (h)	Removal (%)	Reference
UiO-66	Acenaphthene	Not reported (NR)	23.814	0.5	99.7	[192]
ZIF-8	Acenaphthene	NR	14.627	0.5	60.7	[192]
Granular Activated Carbon	Acenaphthylene	Freundlich	31.0	6–8	NR	[193]
	Naphthalene	Freundlich	16.2	6–8	NR	[193]
	Acenaphthene	Freundlich	20.0	6–8	NR	[193]
Rice Husk Activated Carbon	Acenaphthene	Temkin	NR	NR	71.37- 80.56	[194]
Palm Shell Activated Carbon	Acenaphthene	Sips	52.745	1	NR	[195]
Walnut Shell Activated Carbon	Naphthalene	Freundlich	83	0.67	NR	[196]
	Phenanthrene	Freundlich	145	0.67	NR	[196]
Activated Carbon	Fluoranthene	Langmuir	39.98	8	53 %	[197]
Rice husk based activated carbon	Acenaphthene	Temkin	5.554	NR	80.56	[198]

Oil palm leaf activated carbon	Acenaphthene	NR	NR	1.5	98.88	[199]
MnO ₂ nanoparticles	Fluorene	Langmuir	NR	NR	NR	[200]
Ag-GONA beads	Fluorene	Langmuir	67.77	6	53.1	[201]
	Naphthalene	Langmuir	71.93	6	84	[201]
Date pit activated carbon	Fluorene	Freundlich	6.71	10	98.9	[202]
Ammoniation-hydrothermal biochar	Phenanthrene	Freundlich	1.97	24	NR	[203]
Coal-derived carbon nanoparticles	Phenanthrene	Langmuir	1.26	2.5	NR	[204]
	Naphthalene	Langmuir	1.45	2	NR	[204]
MIL-88(Fe)	Anthracene	Langmuir	23.6	25	98.3	[182]
NH ₂ -MIL-88(Fe)	Anthracene	Langmuir	22.2	25	92.4	[182]
Mixed-MIL-88(Fe)	Anthracene	Langmuir	23	25	95.8	[182]
Carbon dots-chitosan-biochar	Anthracene	Langmuir	49.26	60	95	[205]
Magnetic chitosan/graphene oxide	Fluoranthene	Langmuir	28.22	1	90.9	[206]
Natural Sepiolite	Pyrene	Langmuir	8	2	NR	[207]
TiO ₂ @Nanocellulose	Naphthalene	Langmuir	10	2	84.3	[208]
	Pyrene	Langmuir	9.98	2	73	[208]
Green synthesized iron oxide nanoparticles	Pyrene	Langmuir	2.8	2.5	98.5	[209]
	Benzo(a)pyrene	Langmuir	0.029	2.5	99	[209]
sludge-based activated adsorbent	Benzo(a)anthracene	Freundlich	112	5	89	[210]

1.8 Introduction to density functional theory

By the late 1920s, the fundamental principles of quantum mechanics had been firmly established. In a widely cited remark, Paul A. M. Dirac succinctly captured both the success and the limitation of this theoretical framework [211]:

“The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

— P. A. M. Dirac, 1929

This observation highlights a central challenge in electronic structure theory: although the governing laws of quantum mechanics are known, their direct application to realistic many-particle systems leads to equations of prohibitive complexity. As a result, the development of theoretical methods in physics, chemistry, and materials science has focused on constructing physically sound approximations that preserve essential quantum mechanical effects while remaining computationally feasible.

A detailed understanding of the electronic structure of matter is essential for explaining and predicting the physical and chemical properties of materials. While classical physics provides an adequate description of many macroscopic phenomena such as elasticity, thermal transport, and mechanical deformation, it fails fundamentally at the atomic scale [212]. Early experimental findings, including blackbody radiation, the photoelectric effect, atomic emission spectra, and electron diffraction, demonstrated that electrons do not obey classical Newtonian mechanics. Instead, they exhibit distinctly quantum features such as wave–particle duality, interference, and discrete energy levels [213].

One of the most profound shortcomings of classical physics lies in its inability to explain atomic stability [212]. Classical electrodynamics predicts that electrons orbiting a nucleus should continuously radiate energy and eventually collapse into the nucleus, implying that atoms are inherently unstable. Contrary to this prediction, atoms are remarkably stable and possess well-defined electronic energy levels. This stability arises from the quantum mechanical nature of electrons and cannot be understood without a quantum description. In materials, electrons play a decisive role in determining chemical bonding, electrical

conductivity, optical absorption, magnetism, surface phenomena, and catalytic activity. Consequently, a reliable description of electronic behavior is indispensable for the rational design and optimization of novel materials.

At the core of any electronic structure method lies the quantum mechanical description of interacting electrons and atomic nuclei. In principle, all properties of a material can be obtained by solving the many-body Schrödinger equation for this system. However, exact solutions are possible only for the simplest cases. As the number of electrons increases, the dimensionality and complexity of the wavefunction grow exponentially, rendering direct wavefunction-based approaches impractical for realistic materials [214].

Density functional theory provides an alternative and conceptually powerful framework for addressing this problem. Rather than treating the many-electron wavefunction as the fundamental variable, DFT reformulates the quantum mechanical problem in terms of the electron density, which depends only on three spatial coordinates, irrespective of the number of electrons in the system [215]. From a practical perspective, DFT enables the calculation of quantities central to materials research, including total energies, equilibrium structures, charge densities, electronic band structures, and reaction energetics. It is important to emphasize that density functional theory is not empirical in its theoretical foundation. Instead, it is based on exact quantum mechanical theorems, with approximations entering only through the treatment of exchange and correlation effects. This combination of rigorous theoretical grounding while remaining computationally efficient, makes DFT particularly well suited for materials-related problems [216,217].

In the sections that follow, the theoretical foundations of density functional theory are developed in a systematic manner. Beginning with the quantum mechanical many-electron problem and the Born–Oppenheimer approximation, the discussion progresses through mean-field concepts and culminates in the formal framework of DFT.

1.8.1 Schrödinger equation

The theoretical foundation of electronic structure theory is provided by quantum mechanics, which describes the behavior of electrons through the Schrödinger equation [218]. For a

molecular or condensed matter system consisting of nuclei and electrons, the non-relativistic, time-independent Schrödinger equation is written as

$$\begin{aligned}\hat{H}\Psi_i(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) \\ = E_i\Psi_i(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M)\end{aligned}\quad (1.19)$$

where $\hat{H}$ is the Hamiltonian operator, Ψ_i is the many-electron wavefunction, E_i and is the total energy of the system. The wavefunction depends on the spatial and spin coordinates of the N electrons, collectively denoted by $\vec{x}_i$ and on the positions of the M nuclei, denoted by $\vec{R}_A$.

The Hamiltonian operator represents the total energy of the system and consists of kinetic energy terms for electrons and nuclei, as well as potential energy terms arising from electron–electron, electron–nucleus, and nucleus–nucleus Coulomb interactions. In atomic units, it is expressed as

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (1.20)$$

Here, Z_A is the charge of nucleus A , r_{ij} is the distance between electrons i and j , r_{iA} is the distance between electron i and nucleus A , and R_{AB} is the distance between nuclei A and B , M_A is the mass of nucleus A and the Laplacian operator (∇_q^2) is defined as a sum of differential operators.

The wavefunction Ψ contains complete information about the quantum system. All observable properties can, in principle, be obtained from it. This intrinsic complexity motivates the development of approximate approaches for treating many-electron systems, forming the basis for modern electronic structure methods [217].

1.8.2 Born–Oppenheimer approximation

In 1927, Max Born and J. Robert Oppenheimer introduced an approximation to simplify the solution of the many-body Schrödinger equation by exploiting the large difference between nuclear and electronic masses [219]. For instance, the lightest nucleus, the proton (^1H), is approximately 1800 times heavier than an electron, while for a typical nucleus such as carbon

this mass ratio exceeds 20,000. Consequently, nuclei move much more slowly than electrons [217].

This pronounced separation of time scales allows, to a good approximation, the electrons to be treated as moving in the electrostatic field of fixed nuclei. This assumption forms the basis of the Born–Oppenheimer approximation, also known as the clamped-nuclei approximation. Under this approximation, the nuclei are considered stationary; hence, their kinetic energy vanishes and the nucleus–nucleus repulsion contributes only a constant term to the total energy. As a result, the full Hamiltonian given in Equation 1.20 reduces to the so-called electronic Hamiltonian.

$$\hat{H}_{elec} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} \quad (1.21)$$

Solving the corresponding electronic Schrödinger equation,

$$\hat{H}_{elec} \Psi_{elec} = E_{elec} \Psi_{elec} \quad (1.22)$$

yields the electronic wavefunction Ψ_{elec} and the associated electronic energy E_{elec} , which depends on the positions of the nuclei. The total energy of the system is then obtained by adding the classical nucleus–nucleus repulsion energy to the electronic energy i.e.,

$$E_{tot} = E_{elec} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (1.23)$$

Although the Born–Oppenheimer approximation greatly simplifies the quantum mechanical description of molecules by separating the motion of electrons and nuclei, the electronic Schrödinger equation that remains is still very difficult to solve. The electronic wavefunction Ψ_{elec} depends on the positions of all N electrons, meaning it is defined in a space with $3N$ dimensions. In addition, the presence of electron–electron interactions leads to strong correlations between electrons, which further complicates the problem. As a result, even after applying the Born–Oppenheimer approximation, solving the electronic Schrödinger equation exactly is not feasible for most systems, and further theoretical and computational approximations are required [217].

1.8.3 Mean-field approaches: Hartree and Hartree–Fock approximations

A common strategy to treat the many-electron problem is the use of mean-field approximations. In these approaches, the complicated instantaneous interactions between electrons are replaced by an average or effective potential [217]. Each electron is then assumed to move independently in this mean field generated by the nuclei and the remaining electrons. The Hartree and Hartree–Fock approximations represent two closely related mean-field methods.

Hartree approximation

In the Hartree approximation, the many-electron problem is simplified by assuming that each electron moves independently in an average electrostatic field created by the nuclei and the remaining electrons. The electron–electron interaction is treated in a purely classical manner through the charge density [220].

While this approach reduces the many-electron problem to a set of coupled one-electron equations, it neglects the antisymmetry requirement of the electronic wavefunction. As a consequence, the Pauli exclusion principle is not enforced, and exchange effects arising from the indistinguishability of electrons are completely absent. This represents a fundamental limitation of the Hartree model [217].

Hartree–Fock approximation

A few years later, Vladimir Fock extended Hartree’s original idea of representing the many-electron wavefunction as a product of single-particle wavefunctions. In this method, the wavefunction is approximated by an antisymmetrized product of N one-electron wavefunctions [221]. This construction ensures that the Pauli exclusion principle is satisfied and that the wavefunction changes sign upon exchange of any two electrons.

Mathematically, this product is referred to as a Slater determinant, Φ_{SD} [222].

$$\psi_0 \approx \Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{bmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \dots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \dots & \chi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \chi_2(\vec{x}_N) & \dots & \chi_N(\vec{x}_N) \end{bmatrix} \quad (1.24)$$

Or,

$$\Phi_{SD} = \frac{1}{\sqrt{N!}} \det\{\chi_1(\vec{x}_1) \chi_2(\vec{x}_2) \dots \chi_N(\vec{x}_N)\} \quad (1.25)$$

Where, $\chi_i(\vec{x}_i)$ represents spin orbitals and are composed of a spatial orbital $\phi_i(\vec{r})$ and one of the two spin functions, $\alpha(s)$ or $\beta(s)$.

$$\chi_i(\vec{x}_i) = \phi_i(\vec{r})\sigma(s), \quad \sigma = \alpha, \beta. \quad (1.26)$$

Applying the variational principle to the Hartree–Fock wavefunction yields the Hartree–Fock equations,

$$\hat{f} \chi_i = \varepsilon_i \chi_i, \quad i = 1, 2, \dots, N. \quad (1.27)$$

Where, $\hat{f}$ is the Fock operator, defined as

$$\hat{f} = -\frac{1}{2} \nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}} + V_{HF}(i) \quad (1.28)$$

The first two terms represent the kinetic energy of an electron and the potential energy arising from electron–nucleus attraction. The term $V_{HF}(i)$ denotes the Hartree–Fock potential, which replaces the complicated two-electron operator $\frac{1}{r_{ij}}$ in the Hamiltonian with an effective one-electron operator.

However, a critical limitation of the Hartree–Fock approach lies in its treatment of electron correlation. In this framework, each electron is assumed to move in the average electrostatic field created by all other electrons, and exchange effects are incorporated through the antisymmetric nature of the wavefunction [217]. While this mean-field description captures important features of electronic structure, it neglects the instantaneous correlated motion of electrons, which can play a decisive role in determining chemical and material properties.

As a result, the Hartree–Fock energy deviates from the exact non-relativistic energy of the system. For a given basis set, this difference is defined as the correlation energy. The inability of Hartree–Fock theory to recover this correlation energy highlights a fundamental limitation of wavefunction-based mean-field methods. This realization prompted the search for alternative theoretical frameworks capable of incorporating electron correlation more effectively.

1.8.4 Reframing the many-electron problem: The birth of Density Functional Theory

The many-electron wavefunction provides, in principle, a complete quantum-mechanical description of an interacting electronic system. However, this completeness comes at an enormous computational cost. The wavefunction is defined in a $3N$ -dimensional configuration space and therefore contains far more information than is required to describe most ground-state properties of materials [217].

From a practical standpoint, the majority of physically relevant observables such as total energy, charge distribution, electrostatic potential, forces on nuclei, and equilibrium geometries and so on do not depend explicitly on the detailed structure of the many-electron wavefunction. Instead, they are determined primarily by the spatial distribution of electronic charge. This observation implies that, although formally exact, the wavefunction is an excessively detailed descriptor for ground-state properties. The electron density emerges naturally as a more economical quantity. Unlike the wavefunction, the electron density exists in real space and depends only on three spatial coordinates, regardless of system size [215–217].

This insight led to a conceptual breakthrough in 1964, when Hohenberg and Kohn formulated two fundamental theorems establishing a rigorous connection between electron density and energy functionals [223]. Shortly thereafter, Kohn and Sham introduced a practical framework, now known as DFT that made this idea computationally viable [224]. In the Kohn–Sham approach, the electron density, $\rho(\vec{r})$, serves as the central variable for solving the many-electron problem.

The electron density is defined as a multiple integral over the spin coordinates of all electrons and over the spatial coordinates of all electrons except one:

$$\rho(\vec{r}) = N \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 ds_1 d\vec{x}_2 \dots d\vec{x}_N \quad (1.29)$$

Where, the electron density $\rho(\vec{r})$ gives the probability of finding any one of the N electrons within the infinitesimal volume element $d\vec{r}_1$, while the remaining $N-1$ electrons occupy arbitrary positions and spin states in the many-electron state described by Ψ .

By reformulating the quantum-mechanical problem in terms of the electron density, DFT reduces the computational complexity to a level suitable for large molecules, solids, and realistic materials [216,217]. Furthermore, electron–electron correlation effects that are

neglected or only partially treated in Hartree–Fock theory are incorporated, in an approximate but systematic manner, through the exchange–correlation functional. As a result, density functional theory provides a unified framework in which all essential energy contributions are included while retaining practical computational efficiency. In addition, electron–electron correlation effects neglected in the Hartree–Fock method are incorporated within DFT through approximate exchange–correlation functionals, ensuring that all essential energy contributions are included [217].

1.8.5 Hohenberg–Kohn theorems

Density functional theory, in its modern form, originated in 1964 with the publication of a landmark paper by Hohenberg and Kohn in *Physical Review* [223]. The theorems established in this work constitute the fundamental theoretical pillars upon which modern DFT is built.

The first Hohenberg–Kohn theorem

The first theorem states that “the external potential $V_{ext}(\vec{r})$ is (to within a constant) a unique functional of $\rho(\vec{r})$; since, in turn $V_{ext}(\vec{r})$ fixes $\hat{H}$ we see that the full many particle ground state is a unique functional of $\rho(\vec{r})$ ” [217,223]. In other words, the first Hohenberg–Kohn theorem proves that the ground-state energy from Schrödinger’s equation is a unique functional of the electron density. As a result, there exists a one-to-one mapping between the ground-state wave function and the ground-state electron density.

For instance, if we consider two different external potentials $V_1(\vec{r})$ and $V_2(\vec{r})$, that give rise to the same ground-state electron density $\rho(\vec{r})$. The corresponding Hamiltonians, $\hat{H}_1$ and $\hat{H}_2$, therefore have different ground-state wave functions, ψ_1 and ψ_2 , each yielding the same density $\rho(\vec{r})$. Now, invoking the variational principle,

$$E_1^0 < \langle \psi_2 | \hat{H}_1 | \psi_2 \rangle = \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle + \langle \psi_2 | \hat{H}_1 - \hat{H}_2 | \psi_2 \rangle \quad (1.30)$$

i.e.,

$$E_1^0 < E_2^0 + \int \rho(\vec{r}) [V_{ext}^1(\vec{r}) - V_{ext}^2(\vec{r})] \quad (1.31)$$

where E_1^0 and E_2^0 are the ground-state energies of $\hat{H}_1$ and $\hat{H}_2$ respectively. Similarly, an analogous inequality is obtained by interchanging the subscripts. Therefore, by adding these

inequalities and using the fact that both wavefunctions yield the same electron density, one arrives at a contradiction:

$$E_1^0 + E_2^0 < E_2^0 + E_1^0 \quad (1.32)$$

This contradiction establishes that no two different external potentials can correspond to an identical ground-state electron density (ρ_0), demonstrating that the ground-state density uniquely specifies the external potential V_{ext} .

Since the total ground-state energy is a functional of the ground-state electron density, each of its individual components must also be functionals of the density, and the total energy may therefore be written as

$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{Ne}[\rho_0] \quad (1.33)$$

By separating the total energy expression into terms that depend on the actual system, including the electron–nucleus interaction energy ($E_{Ne}[\rho_0] = \int \rho_0(\vec{r}) V_{Ne} d\vec{r}$) and those which are universal and independent of N , R_A and Z_A , we obtain

$$E_0[\rho_0] = \int \rho_0(\vec{r}) V_{Ne} d\vec{r} + T[\rho_0] + E_{ee}[\rho_0] \quad (1.34)$$

Or,

$$E_0[\rho_0] = \int \rho_0(\vec{r}) V_{Ne} d\vec{r} + F_{HK}[\rho_0] \quad (1.35)$$

Where the independent parts result in a new quantity called the Hohenberg-Kohn functional. If $F_{HK}[\rho_0]$ is evaluated for an arbitrary electron density $\rho(\vec{r})$, it yields the expectation value $\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$ which corresponds to the sum of the kinetic energy and the electron–electron interaction energy, with the ground-state wave function Ψ corresponding to that density.

This $F_{HK}[\rho_0]$ is regarded as the holy grail of DFT [217]. If it were known exactly, the Schrödinger equation would be solved exactly rather than approximately.

The second Hohenberg–Kohn theorem

Although the first Hohenberg–Kohn theorem proves that a functional of the electron density exists that can, in principle, be used to solve the Schrödinger equation, it does not specify the

explicit form of this functional. The second Hohenberg–Kohn theorem establishes an important property of the functional: The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation [215–217]. In simple terms, this theorem states that the Hohenberg-Kohn functional $F_{HK}[\rho]$, which yields the ground-state energy of a system, attains its minimum value if and only if the input density corresponds to the true ground-state density, ρ_0 .

$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + E_{Ne}[\tilde{\rho}] + E_{ee}[\tilde{\rho}] \quad (1.36)$$

Any trial electron density must satisfy two fundamental conditions. First, since it represents a probability density, it must be non-negative everywhere in space, i.e., $\tilde{\rho}(\vec{r}) \geq 0$. Second, it must satisfy the conservation principle $\int \tilde{\rho}(\vec{r}) d\vec{r} = N$, where N is the total number of electrons in the system [217]. For any density satisfying these conditions and associated with a given external potential $\tilde{V}_{ext}$ the energy obtained from the functional in Equation 1.33 provides an upper bound to the true ground-state energy E_0 . E_0 is achieved if and only if the exact ground-state density is substituted into Equation 1.35.

Further, the explicit form of the kinetic energy functional ($T[\tilde{\rho}]$) for an interacting many-electron system is not known. Consequently, the direct minimization of the total energy functional with respect to the electron density becomes complicated. This difficulty was overcome by the seminal work of Kohn and Sham, who made it possible [224].

1.8.6 Kohn-Sham equations

The Hohenberg–Kohn theorems establish that the ground-state energy of an interacting many-electron system can be written as a functional of the electron density. However, the explicit form of the kinetic energy functional of an interacting system is unknown, which makes a direct minimization of the total energy functional impractical. In early density functional methods such as the Thomas–Fermi model, the kinetic energy was described only approximately [215–217,225]. This poor description limited the accuracy of DFT and prevented it from being used as a reliable quantitative tool for a long time. This problem was later resolved by Kohn and Sham in 1965. They proposed a method in which most of the kinetic energy is treated exactly by introducing a reference system of non-interacting electrons that has the same electron density as the real interacting system. The exact kinetic energy of this non-interacting system

can be calculated directly, while the remaining interaction effects are included in the exchange–correlation term.

The ground-state energy of a system may be written as

$$E_0 = \min_{\rho \rightarrow N} (F[\rho] + \int \rho(\vec{r}) V_{Ne} d\vec{r}) \quad (1.37)$$

where the universal functional $F[\rho]$ includes the contributions from the kinetic energy, the classical Coulomb interaction between electrons, and the non-classical terms arising from self-interaction correction, exchange and electron correlation effects.

$$F[\rho(\vec{r})] = T[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{ncl}[\rho(\vec{r})] \quad (1.38)$$

The functional $J[\rho(\vec{r})]$ is known; however, obtaining accurate expressions for the kinetic energy functional $T[\rho(\vec{r})]$ and the non-classical interaction term $E_{ncl}[\rho(\vec{r})]$ remains a major challenge. To address this difficulty, the Kohn–Sham method represents the kinetic energy and the electron density in terms of a reference system of non-interacting electrons as

$$T_s = -\frac{1}{2} \sum_i^N \langle \psi_i | \nabla^2 | \psi_i \rangle \quad (1.39)$$

And,

$$\rho_s(\vec{r}) = \sum_i^N \sum_s |\psi_i(\vec{r}, s)|^2 = \rho(\vec{r}) \quad (1.40)$$

where ψ_i are the orbitals of the non-interacting reference system and are referred to as the Kohn–Sham orbitals. Although this reference system is constructed to reproduce the same electron density as the real interacting system, its kinetic energy is not equal to the true kinetic energy of the interacting electrons, i.e., $T_s \neq T$. Kohn and Sham accounted for this difference by introducing the following separation of the universal functional $F[\rho]$:

$$F[\rho(\vec{r})] = T_s[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})] \quad (1.41)$$

where E_{xc} , known as the exchange–correlation energy, is defined as

$$E_{xc}[\rho] \equiv (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]) \equiv T_c[\rho] + E_{ncl}[\rho] \quad (1.42)$$

The effective external potential V_S is now defined such that it yields a Slater determinant with the same electron density as the real interacting system. By incorporating the separation introduced in Equation 1.41, the total energy of the interacting system can be expressed as

$$E[\rho(\vec{r})] = T_S[\rho] + J[\rho] + E_{XC}[\rho] + E_{Ne}[\rho] \quad (1.43)$$

$$\begin{aligned} &= T_S[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{XC}[\rho] + \int V_{Ne}\rho(\vec{r})d\vec{r} \\ &= -\frac{1}{2} \sum_i^N \langle \psi_i | \nabla^2 | \psi_i \rangle + \frac{1}{2} \sum_i^N \sum_j^N \iint |\psi_i(\vec{r}_1)|^2 \frac{1}{r_{12}} |\psi_j(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 \\ &\quad + E_{XC}[\rho(\vec{r})] - \sum_i^N \int \sum_A^M \frac{Z_A}{r_{1A}} |\psi_i(\vec{r}_1)|^2 d\vec{r}_1 \end{aligned} \quad (1.44)$$

Among all the terms in the energy functional, the exchange–correlation energy E_{XC} is the only term for which no explicit expression is known and therefore represents the main unknown of the theory. By applying the variational principle, the following equations are obtained which are called Kohn Sham equation:

$$\left(-\frac{1}{2} \nabla^2 + \left[\int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}) - \sum_A^M \frac{Z_A}{r_{1A}} \right] \right) \psi_i = \left(-\frac{1}{2} \nabla^2 + V_{eff}(\vec{r}) \right) \psi_i = \varepsilon_i \psi_i \quad (1.45)$$

By comparing the above equation with the one-particle equations of the non-interacting reference system, it becomes evident that the term enclosed in square brackets, namely the effective potential V_{eff} , is identical to the Kohn–Sham potential V_S .

$$V_S(\vec{r}) \equiv V_{eff}(\vec{r}) = \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}) - \sum_A^M \frac{Z_A}{r_{1A}} \quad (1.46)$$

Where, V_{XC} is the potential due to the exchange–correlation energy E_{XC} and is defined as the functional derivative of E_{XC} with respect to ρ , i. e.,

$$V_{XC} \equiv \frac{\delta E_{XC}}{\delta \rho} \quad (1.47)$$

Thus, once all the terms in Equation 1.46 are known, the Kohn–Sham potential V_s can be constructed and inserted into the one-electron Kohn–Sham equations. Solving these equations yields the Kohn–Sham orbitals, from which the ground-state electron density and the ground-state energy can be obtained using the energy expression given in Equation 1.44. As a result, similar to the Hartree–Fock method, the Kohn–Sham equations must be solved using an iterative self-consistent procedure [217].

1.9 Review of DFT studies on adsorption mechanisms and surface interactions

Density Functional Theory (DFT) has emerged as a powerful theoretical framework for rational materials design, enabling the prediction of adsorption behavior, identification of active sites, and elucidation of microscopic interaction mechanisms prior to experimental validation, as well as serving to corroborate and rationalize experimental findings. These theoretical insights guide experimental efforts by narrowing down promising material compositions and surface modifications, thereby accelerating the development of high-performance materials for specific applications. Some representative reports from the literature demonstrating this approach are discussed below:

Shanmugam et al. [226] employed DFT to investigate the adsorption of Li^+ , Na^+ , and K^+ ions on BN-codoped and S-doped pristine and divacancy-defected graphene sheets to understand the role of doping and defects in enhancing ion adsorption for battery applications. Their results showed that adsorption is most favorable at the hollow site and that divacancy-defected structures significantly improve adsorption strength, with S-doped DV-graphene exhibiting the highest adsorption energy (up to -3.55 eV for Li^+). Electronic structure calculations revealed increased HOMO–LUMO gaps and noticeable DOS shifts upon ion adsorption, particularly for Li^+ on defected sheets, suggesting enhanced electronic stability. The calculated storage capacity reached $82.958 \text{ mAh g}^{-1}$ for Li^+ on BN-codoped DV-graphene, demonstrating that defect and dopant engineering effectively enhances adsorption and electrochemical performance.

In another report, Yan and colleagues [227] performed a DFT investigation to explore the adsorption behavior of SF_6 on Pd-doped hydroxyl-terminated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ($\text{Pd@Ti}_3\text{C}_2(\text{OH})_2$) with the aim of assessing its catalytic suitability for SF_6 degradation. The optimized geometrical configurations revealed elongation and subsequent breaking of S–F

bonds, accompanied by the formation of new Pd–F and Pd–S bonds, indicating activation of the SF₆ molecule. Furthermore, analysis of the total density of states (DOS) and partial density of states (PDOS) showed pronounced orbital hybridization between Pd-4d and F-2p states near the Fermi level, confirming strong chemisorption and electronic interaction between the adsorbate and substrate. These findings demonstrated that Pd incorporation significantly enhances the surface reactivity of Ti₃C₂(OH)₂, thereby identifying Pd@Ti₃C₂(OH)₂ as a promising catalytic material for SF₆ decomposition.

In a separate study, Zhou et al. [228] reported a combined experimental and DFT study on VOC adsorption over activated carbon/metal oxide (AC/MO_x; M = Mg, Zn, Cu, Zr) composites prepared via an evaporation-induced self-assembly method. DFT study revealed that acetone and methanol exhibit significantly stronger adsorption affinities toward metal oxide surfaces than toluene, in agreement with experimental observations. The enhanced interaction of acetone and methanol is attributed to the combined effect of dative bonding and hydrogen bonding with surface sites. Moreover, adsorption behavior is influenced by the polarity and molecular structure of the adsorbates, as well as the Lewis acid–base characteristics of the metal oxide surface.

Moreover, DFT has been extensively employed to elucidate the influence of heteroatom doping and surface functionalization on the adsorption performance of carbon-based materials. For instance, DFT calculations demonstrated that Ge- and Cr-doped graphene exhibit significantly enhanced adsorption energies and charge transfer toward H₂ and C₂H₂ compared to pristine graphene, owing to the creation of new active sites and modified electronic structures [229]. Similarly, investigations on fullerene-based systems revealed that mono- and co-doping with transition metals (Ni, Cu, Fe, and Zn) substantially improved the adsorption strength and sensing performance toward benzene and formaldehyde through modulation of frontier orbitals and adsorption energetics [230].

Surface functionalization with oxygen-containing groups has also been shown to play a crucial role in adsorption enhancement. DFT studies on carbonaceous materials reported that carbonyl, carboxyl, hydroxyl, and lactone groups significantly alter electron density distribution, increase surface polarity, and strengthen electrostatic interactions and hydrogen bonding with adsorbates [231]. In the case of alkali-modified biochar, DFT analysis further verified that specific functional groups (e.g., –COOH) strongly interact with dye molecules, such as

methylene blue through electrostatic attraction and π – π interactions, leading to improved adsorption capacity [232].

Additionally, adsorption of PAHs on graphene was shown to be governed predominantly by π – π stacking and van der Waals interactions, with adsorption strength increasing with molecular size, highlighting the role of the delocalized π -electron system of carbon frameworks [233]. Furthermore, studies on emerging two-dimensional materials such as B₂N monolayers demonstrated that electronic structure modulation significantly influences gas adsorption energy, sensitivity, and recovery characteristics, reinforcing the importance of theoretical screening in adsorbent design [234].

1.10 Aim and objectives

Based on the background and literature survey presented in the preceding section, the primary aim of this research is to develop efficient synthesis strategies for preparing functionalized graphene derivatives and to systematically investigate their potential in sustainable energy storage and environmental remediation through combined experimental and theoretical approaches.

To achieve this aim, the following specific objectives are proposed:

- To develop efficient synthesis and surface functionalization methods for graphene derivatives and to characterize the resulting materials.
- To evaluate the electrochemical performance of functionalized graphene-based electrode materials for supercapacitor applications using ionic liquid-based electrolytes, with the objective of achieving an expanded operating voltage window and enhanced energy density.
- To investigate the adsorption behavior of functionalized graphene-based materials toward selected environmental pollutants and to establish correlations between surface functionalization and adsorption efficiency.
- To employ density functional theory (DFT) calculations to understand the effects of heteroatom doping in graphene and to elucidate the role of functionalization in enhancing adsorption performance.

1.11 Thesis structure

The thesis consists of eight chapters. Each chapter is briefly summarized below:

Chapters	Title	Summary
1	Introduction and literature review	This chapter provides the background of the research along with the problem statement. It presents the history and development of graphene, supercapacitors, and the fundamentals of Density Functional Theory (DFT) and adsorption processes. The aims and objectives of the study are also discussed.
2	Characterization Techniques	This chapter describes the various characterization techniques employed in this work, including X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and electrochemical measurements.
3	DFT study on the structural, optical and electronic properties of platinum group doped graphene	This chapter presents a detailed investigation of how doping with platinum group metals influences the structural, optical, and electronic properties of graphene.
4	Scalable one-pot synthesis of aminated reduced graphene oxide for high-performance supercapacitor electrodes	This chapter introduces a novel and scalable one-pot synthesis route for aminated graphene that bypasses the conventional graphene oxide synthesis

		process. The electrochemical performance of the synthesized material is evaluated and compared with its non-aminated counterpart.
5	(i) Ultrafast, Green Synthesis of Bromographene for High-Energy Supercapacitors	This section reports an environmentally friendly method for synthesizing brominated reduced graphene oxide. The material is extensively characterized and used to fabricate a high-performance supercapacitor demonstrating high energy density.
	(ii) A Comparative Study on the Bromination of Reduced Graphene Oxide Using Different Tribromides	This section extends the previous study by comparing the bromination efficiency of five different tribromide reagents. After developing a greener bromination strategy, we systematically compared the bromination efficiency and identified the most effective brominating agent.
6	A 3.2 V Dual-Functionalized Graphene Supercapacitor with High Energy Density and Wide Temperature Tolerance for Regenerative Energy Storage Applications	This chapter reports the development of a dual-functionalized graphene system obtained through simultaneous bromine and nitrogen functionalization. The material is used to fabricate a 3.2 V supercapacitor and its application in capturing regenerative braking energy is demonstrated using a model system.
7	NH ₂ -functionalized reduced graphene oxide as a high-performance adsorbent	This chapter discusses the synthesis and application of amine-

	for naphthalene: A combined experimental and DFT study	functionalized reduced graphene oxide (aminated graphene) for the removal of naphthalene as a model polycyclic aromatic hydrocarbon (PAH). Along with experimental studies, molecular-level insights into the adsorption mechanism are obtained using DFT calculations.
8	Summary and future directions	This chapter summarizes the major findings of the research and discusses potential future research directions and applications.

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Chapter 2



Characterization techniques

CHAPTER 2

Characterization techniques

Detailed characterization is an essential part of material preparation and evaluation, as it provides fundamental insights into the structural, morphological, and compositional features of the synthesized materials. A comprehensive set of analytical techniques was employed in this work to systematically examine their physicochemical and electrochemical properties. This chapter outlines the characterization techniques used to evaluate the physicochemical and electrochemical properties of the synthesized materials.

2.1 X-ray Diffraction

2.1.1 Principle

X-ray diffraction (XRD), also known as the Debye and Scherrer method, is a non-destructive analytical technique used to determine the phase of a material whether it is a polycrystalline or amorphous in both powder and solid forms. It is a commonly employed technique for both qualitative and quantitative analysis, where qualitative analysis involves two theta angles, peak intensity and lattice parameters, while quantitative analysis includes phase identification, phase composition (percentage), crystalline size, orientation and other structural details [1].

XRD works on the principle of diffraction of light through the crystal lattice of a material, where diffraction of light by lattices or crystals occur when the diffraction comes from a distance that has a wavelength comparable to the distance (approximately 1 Å) between atoms. X-rays, which are high-energy photons with wavelengths ranging from about 0.5 to 2.5 Å, are commonly used as the radiation source. When an X-ray beam interacts with a material, part of the beam is absorbed or transmitted, while the remaining portion is scattered and diffracted, this scattered diffraction is what XRD detects. Some of the scattered X-ray beam have different phases, so they cancel each other out and do not produce a detectable signal. However, some scattered X-rays have the same phase, so they reinforce each other. The reinforced diffraction beams form a unique pattern of peaks when detected. This pattern is specific to the atomic arrangement of the material and therefore acts like a fingerprint, allowing the material to be identified [2].

Figure 2.1 shows the basic principle of XRD based on Bragg's law. When a monochromatic X-ray beam is incident on a crystalline material, it interacts with a series of parallel atomic planes separated by an interplanar spacing d , as shown in the Figure 2.1.

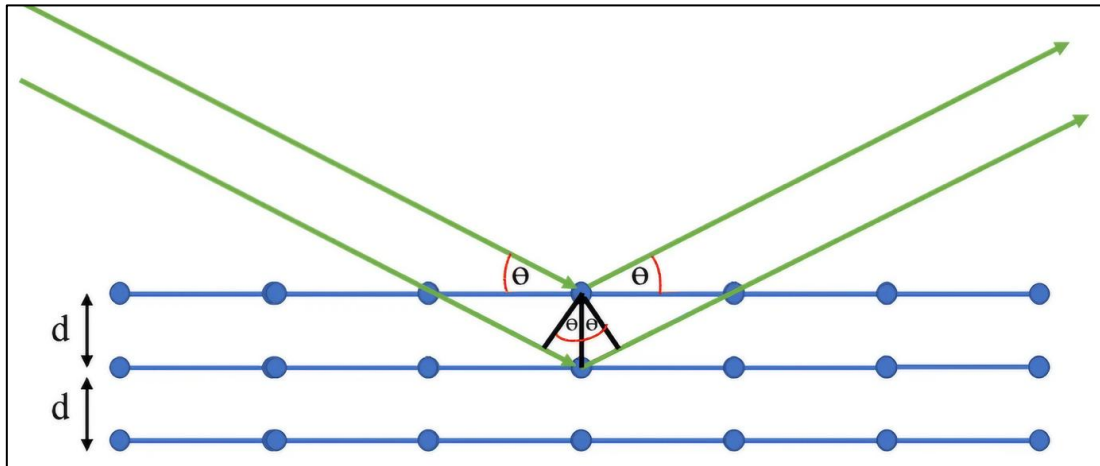


Figure 2.1. Schematic diagram illustrating Bragg's law. Reproduced with permission from Ref. [3].

Two incident X-ray waves strike two successive atomic planes at an angle θ . One wave is reflected from the upper atomic plane, while the second wave penetrates deeper into the crystal and is reflected from the lower atomic plane. As indicated in the figure, the angle of incidence is equal to the angle of the reflection (θ). Since the second wave travels to a lower plane before being reflected, it covers a longer distance compared to the wave reflected from the upper plane. This difference in travel distance creates a path difference between the two reflected waves. From the geometry of the arrangement shown in the figure, the total additional distance travelled by the second wave is equal to $2d \sin \theta$.

Constructive interference occurs only when this path difference is equal to an integral multiple of the wavelength (λ) of the incident X-rays. If n is the order of reflection ($n = 1, 2, 3$), the condition for diffraction is given by

$$n\lambda = 2d \sin \theta \quad (2.1)$$

This relationship is known as Bragg's law [4]. Where n is the order of diffraction, λ is the wavelength of the incident X-rays, d is the distance between crystallographic planes with specific Miller indices (hkl), and θ is the angle of incidence. When this condition is met, distinct diffraction peaks are observed at specific 2θ values. The resulting diffraction pattern, consisting of peaks with varying intensities, depends on the crystal structure, lattice parameters and atomic arrangement within the unit cell, making XRD a reliable technique for identifying and characterizing crystalline materials [5].

2.1.2 Instrumentation / Construction and working

Figure 2.2 illustrates the basic instrumentation of a XRD system. A typical powder XRD instrument consists of an X-ray source, a sample holder mounted on a goniometer, and a detector assembly. In most laboratory scale diffractometers, X-rays are generated inside a sealed X-ray tube using a heated tungsten filament (Cathode), which emits electrons through thermionic emission.

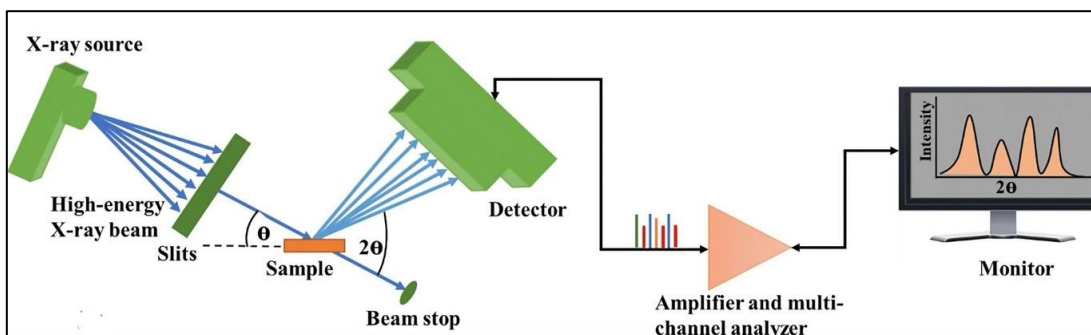


Figure 2.2. Schematic representation of a typical X-ray diffraction (XRD) instrument showing the X-ray source, incident beam optics, sample stage, and detector assembly. Reproduced with permission from Ref. [3].

These electrons are accelerated under a high voltage (typically 30-60 kV) toward a metal anode. When the high energy electrons hit the metal anode, characteristic X-ray radiation is produced due to electronic transition within the anode. This metal anode can be made up of elements such as Cu, Cr, Fe, Co, Mo, or Ag depending on the desired wavelength of X-ray radiation being used. Among these, Cu K α radiation with a wavelength of approximately 1.5406 Å, in particular is most widely used in powder

XRD studies. A sample, usually in powdered or polycrystalline form, is put in a sample holder and placed at the center of a goniometer, which precisely controls the incident and diffracted angles in a θ - 2θ geometry. A detector is used to measure the intensity of diffracted X-rays at various diffraction angles, generating the diffraction pattern used for material identification and structural analysis [1,6].

In powder XRD, the crystals are randomly positioned, enabling all possible crystal planes to meet the requirement of Bragg's law during the scan process. This, in turn, enables a full diffraction data spectrum to be collected, including a number of distinct peaks positioned at particular 2θ angles. The peak position, intensity, and width of these peaks provide information about the crystal structure, lattice parameters, crystallinity and microstructural features of the material [5]. Sharp and intense diffraction peaks indicate a well ordered crystalline structure, whereas broad peaks or diffuse patterns suggest poor crystallinity or amorphous nature. Changes in peak position and intensity reflect variations in lattice spacing, strain, defects or preferred orientation in the material.

2.1.3 Information obtained from XRD

- **Phase Identification:** Every crystal phase has its own distinct diffraction peak pattern, making it possible to identify by matching it to a reference card available in JCPDS or ICDD.
- **Crystal structure and crystallinity:** The presence or absence of sharp diffraction peaks allows differentiation between crystalline and amorphous phases, as well as assessment of the degree of crystallinity.
- **Lattice parameters and interplanar spacing:** Precise determination of d -spacing and unit cell dimensions can be achieved from peak positions.
- **Crystallite size:** XRD is also useful for estimating the size of crystallites in a material, which is of particular significance in nanostructured materials. The average size of crystallites (D) in a material can be calculated using the full-width at half-maximum (FWHM) intensity of a diffraction peak, given by the Scherrer formula [1]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2.2)$$

- Here, K is the Scherrer shape factor, generally assumed to be about 0.9 depending on the shape of the crystallites, λ is the wavelength of the incident X-ray, β is the full-width at half-maximum of the diffraction peak in radians, and θ is the Bragg's angle.
- **Structural modifications:** XRD can detect phase transformations, lattice distortions, and structural changes induced by synthesis conditions, thermal treatment, or chemical functionalization.

2.2 X-ray Photoelectron Spectroscopy

2.2.1 Principle

X-ray photoelectron spectroscopy (XPS) is a surface sensitive analytical technique in which X-rays irradiate the surface of a material and the kinetic energy of emitted electrons is measured. The two most important features that make XPS a powerful characterization tool are its high surface sensitivity and its ability to assess elemental composition of surfaces and interfaces, chemical states, and bonding structure of materials [7,8]. The technique is based on the photoelectric effect, which was first observed by Heinrich Hertz in 1887, when he reported the emission of electrons from surfaces exposed to light. The phenomenon was later explained quantitatively by Albert Einstein in 1905, for which he was awarded the Nobel Prize in Physics in 1921. The emission of electrons under X-ray irradiation was subsequently demonstrated by Robinson and Rawlinson in 1914, and the first use of photoemission as an analytical method was reported by Steinhardt and Serfass in 1951. The systematic development of X-ray photoelectron spectroscopy into a reliable and high-resolution surface analysis technique was carried out by Kai Siegbahn and his collaborators at the University of Uppsala during the 1950s and 1960s. Their work established the foundations of modern XPS, initially known as electron spectroscopy for chemical analysis (ESCA) and was recognized with the Nobel Prize in Physics in 1981 [9].

On the basis of this principle, XPS employs high energy X-ray radiation to interact with the atoms present at the surface of material that can eject core level electrons on the basis when the photon energy is greater than the energy holding the electrons inside the atom. These emitted electrons are known as photoelectrons [10]. The mechanism of photoelectric effect is shown in Figure 2.3. When monochromatic X-ray radiation ($E = h\nu$) strikes an atom, it can eject a core level electron from the K, L or M shell if the photon energy is greater than the binding energy of that electron. The emitted electrons, known as a photoelectron leaves the atom with a certain kinetic energy. The ejection of this electron creates a vacancy in the inner shell, which is subsequently filled by an electron from a higher energy level. The relaxation process results in the release of excess energy either in the form of characteristic X-ray radiation or through the emission of an Auger electron, as shown in the Figure 2.3.

The photoemission process follows the law of energy conservation. The energy of the incident X-ray photon utilized partly to overcome the binding energy (BE) of the electron and the remaining energy appears as the kinetic energy (KE) of the emitted photoelectron. The relationship is expressed as:

$$h\nu = BE + KE + \phi \quad (2.3)$$

where $h\nu$ represents the energy of the incident X-ray photon, where h is the Planck's' constant and ν is the frequency of the X-ray radiation. BE is the binding energy of the electron, KE is the kinetic energy of the emitted photoelectron, ϕ is the work function of the spectrometer, a constant value [11]. Since the X-ray energy ($h\nu$) and the spectrometer work function (ϕ) are known quantities, and the kinetic energy (KE) of the emitted electron is experimentally measured, the binding energy (BE) of the electron can be calculated. The binding energy is referenced to the Fermi level of the sample and is independent of the X-ray source used. Each element has a unique set of binding energies corresponding to its core electron orbitals, such as 1s, 2p, or 3d levels. When photoelectrons originating from these orbitals are detected, they appear as peaks in the XPS spectrum [12].

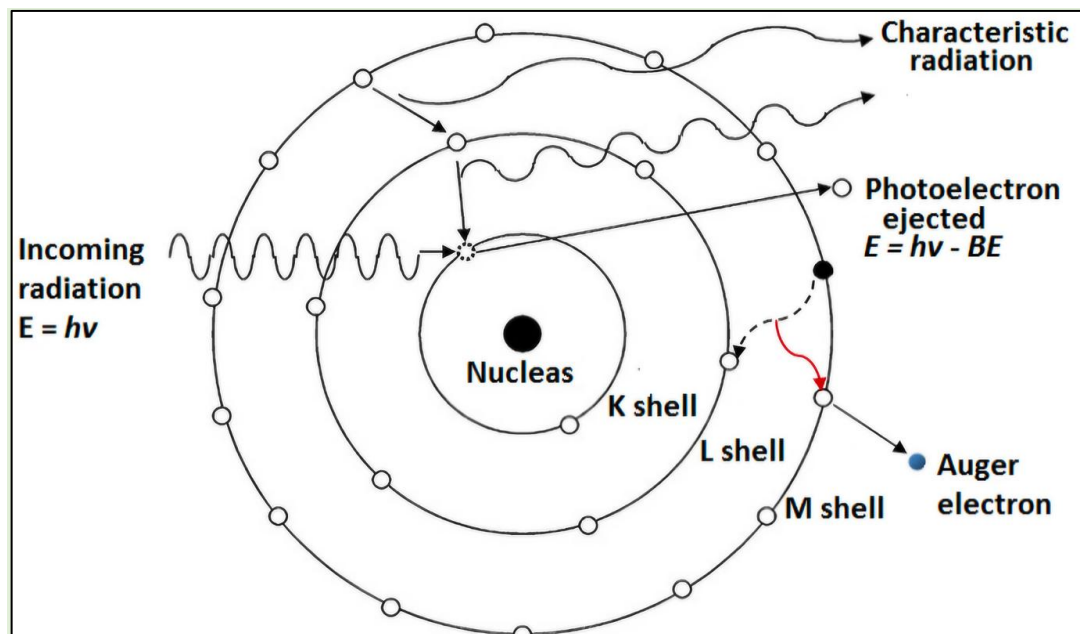


Figure 2.3. The mechanism of photoelectron generation. Reproduced with permission from Ref. [39].

This is why XPS spectra are typically presented on a binding energy scale and the position of each peak identifies the element present on the surface. Furthermore, the binding energy of a core electron is influenced by the chemical environment of the atom. Changes in oxidation state, bonding, or coordination alter the local electron density around the atom, which in turn slightly shifts the binding energy of the emitted electrons. These shifts, known as chemical shifts, enable XPS distinguish between different chemical states of the same element, for instance metal and oxide forms or different functional groups in carbon-based materials.

Although X-rays can penetrate deeply into solid, the emitted electrons have a very limited escape depth due to inelastic scattering processes within the material. Only electrons generated within the top few nanometres of the surface can escape without significant energy loss and contribute to the characteristic XPS peaks. Electrons originating from deeper regions lose energy through collisions and form a background signal rather than sharp peaks. As a result, XPS is inherently surface sensitive, typically probing the top 5 to 10 nm of the material surface [12].

2.2.2 Instrumentation/ Construction and working

A basic setup for XPS involves four main elements: an X-ray source, an ultra-high vacuum (UHV) chamber, an electron energy analyser, and an electron detector system, as demonstrated in Figure 2.4. All XPS instruments operate under ultra-high vacuum conditions, typically with base pressures in the range of 10^{-5} mbar and 10^{-6} mbar. The use of UHV is critical for two main reasons. First, photoelectrons emitted from the sample surfaces must reach the energy analyzer without undergoing scattering by residual gas molecules, which requires pressure of 10^{-5} mbar and 10^{-6} mbar. However, in actual operation, most XPS system maintain significantly lower base pressures, typically in the range of 10^{-9} to 10^{-10} mbar. Second, because XPS probes only the near-surface region, the technique is extremely sensitive to surface contamination. Consequently, the use of an UHV environment is essential to suppress surface contamination inside the analysis chamber.

The X-ray source is responsible for generating the photons that induce photoemission. The most common X-ray sources are Al K α (1486.6 eV) and Mg K α (1253.6 eV), with aluminium sources being more widely used in modern instruments. X-rays are produced by accelerating electrons from a heated filament (typically tungsten or LaB₆) toward a metal anode. When the high energy electrons strike the anode, characteristics X-rays are generated. The choice of anode material determines the photon energy and influences the depth of analysis, ionization probability and spectral resolution [13].

Between the sample and the analyzer, a series of electrostatic extraction lenses is used to collect and focus the emitted photoelectrons. These lenses control the acceptance angle and determine the region of the sample surface from which electrons are collected. The extraction lenses also retard the kinetic energy of the electrons to a user defined value known as the pass energy before they enter the analyzer. Lower pass energies provide higher resolution and are used for high resolution core level spectra, whereas higher pass energies allow greater electron throughput and are typically used for survey scans. The kinetic energy of the emitted electrons is measured using an electron energy analyzer, most commonly a concentric hemispherical analyzer (CHA).

This analyzer consists of two hemispheres with different applied voltages. Electrons enter the analyzer through a slit, and only electrons with a specific kinetic energy can travel through the analyzer.

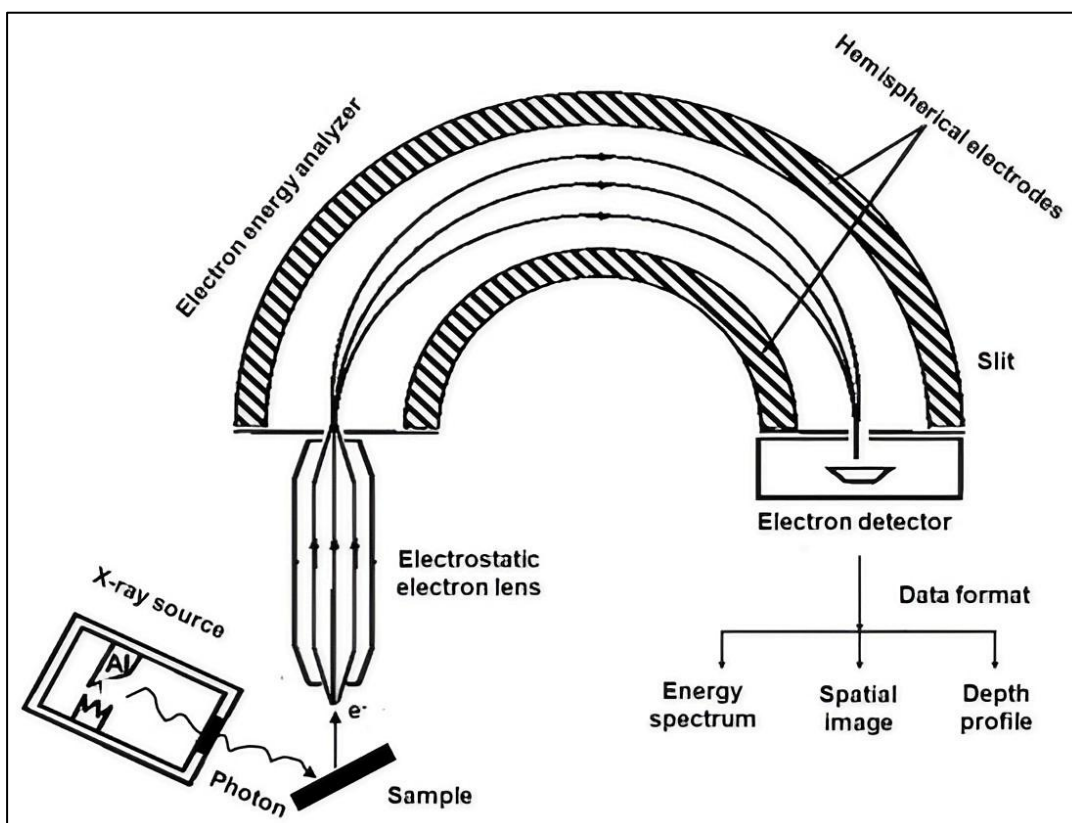


Figure 2.4. Schematic diagram of the instrumentation of an X-ray Photoelectron Spectroscopy (XPS), illustrating the X-ray source (commonly Al $K\alpha$ or Mg $K\alpha$), ultra-high vacuum (UHV) chamber, sample holder, electron energy analyzer (hemispherical analyzer) and detector. Reproduced with permission from Ref. [40].

Electrons with higher kinetic energy collide with the outer hemisphere, while electrons with lower kinetic energy collide with the inner hemisphere. By adjusting the voltages applied to the hemispheres, electrons of different kinetic energies can be selectively transmitted. The energy resolution of the analyzer depends on various factors such as radius of the analyzer, with larger radius analyzers providing better energy resolution, source linewidth, analyzer radius, etc. After the energy analysis, the transmitted electrons are detected using an electron multiplier, such as a channel electron multiplier or a multichannel plate detector. These detectors amplify the electron signal and convert it into a measurable electrical signal. Many modern instruments use

position sensitive detectors, which allow simultaneous detection of electrons over a range of energies, improving data collection efficiency and reducing acquisition time. The detected signal intensity is recorded as a function of electron kinetic energy and later converted to binding energy to generate the XPS spectrum [14,15].

2.2.3 Information obtained from XPS

XPS provides a wide range of qualitative and quantitative information related to the surface chemistry of materials:

- **Elemental composition:** By their characteristic binding energies, XPS can detect all elements present on the surface of a material, except hydrogen and helium.
- **Chemical state-oxidation state analysis:** Chemical shifts enable the differentiation of an element's various oxidation states and bonding environments, which is very relevant to functionalized and composite materials.
- **Quantitative surface analysis:** The relative intensities of the peaks can be utilized to estimate the atomic concentration of elements present on the surface and, therefore, allow semi-quantitative compositional analysis.
- **Surface sensitivity:** Due to its limited information depth, XPS selectively probes the outermost surface layers, making it highly effective for studying surface functionalization, adsorption, and interfacial phenomena.
- **Chemical bonding and surface modification:** XPS is particularly useful for confirming chemical functionalization, doping, or surface modification by identifying new bonding environments and changes in elemental composition after chemical treatment.

2.3 Field Emission Scanning Electron Microscopy

2.3.1 Principle

Field Emission Scanning Electron Microscopy (FE-SEM) is an advanced surface imaging technique that employs a focused electron beam instead of visible light to achieve high-resolution visualization of material surfaces. Owing to the extremely short wavelength of electrons, FE-SEM offers significantly higher magnification and spatial resolution compared to optical microscopy, typically in the range of ~ 10 to $300,000\times$ [16].

FE-SEM operates on the principle of electron–matter interaction, where a finely focused, high-energy electron beam is scanned across the sample surface. The distinctive feature of FE-SEM is the use of a field-emission electron source, which generates a highly coherent and intense electron beam with a very small probe size. This enables exceptional resolution and improved image clarity, particularly for nanostructured and low-dimensional materials. When the incident electron beam interacts with the sample surface, several signals are generated as a result of elastic and inelastic scattering processes. These include secondary electrons, backscattered electrons, and characteristic X-rays, each carrying specific information related to surface morphology and composition [17].

2.3.2 Instrumentation / Construction and working

A typical FE-SEM instrument consists of a field-emission electron gun, electromagnetic lens system, scanning coils, specimen stage, various detectors (secondary electron, backscattered electron and X-ray detector), and a computer-based control unit. A schematic diagram of FE-SEM image is illustrated in Figure 2.5.

The electron gun is the core component of FE-SEM and comprises a sharp metallic tip, commonly made of tungsten or a single-crystal material. Under the application of a strong electric field, electrons are extracted from the tip surface and accelerated to form a highly focused electron beam. The electromagnetic lens system, including

condenser lenses and an objective lens, is used to control the beam diameter and focus it into a fine probe on the sample surface. Scanning coils deflect the beam in a raster pattern across the specimen. A sample stage helps in placing and adjusting a sample in various directions. FE-SEM analysis is done in a high vacuum to eliminate unwanted scattering of electrons to ensure smooth propagation of the beam. A combination of various detectors, such as secondary detectors, backscattered detectors, and energy dispersive X-ray analyzers, is arranged around the sample to detect signals emitted during analysis. The entire system is controlled via dedicated software that regulates beam parameters and image acquisition [18].

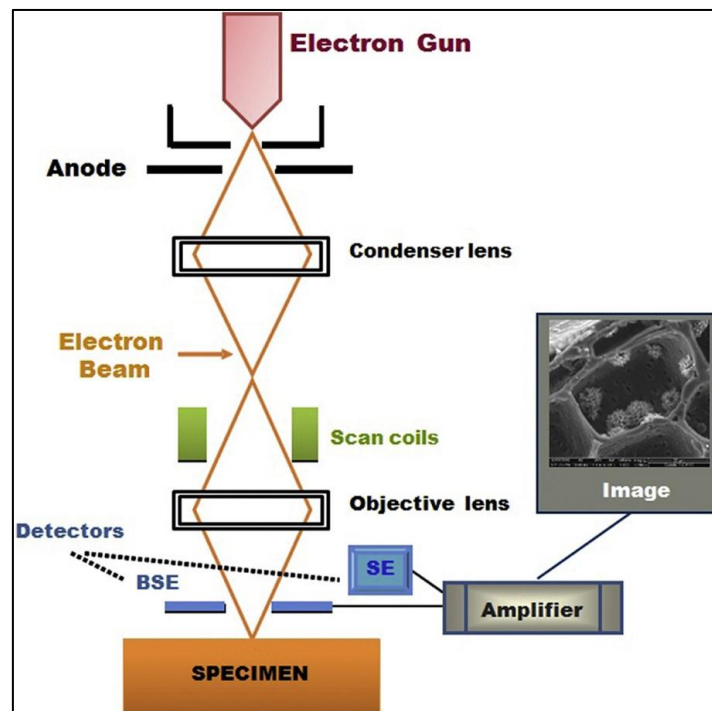


Figure 2.5. Schematic diagram of a Field Emission Scanning Electron Microscope (FESEM) used for high-resolution surface imaging and compositional analysis. Reproduced with permission from Ref. [41].

In FE-SEM analysis, a highly focused beam of electrons produced by the field emission source is projected on the surface of the specimen. During the interaction of the primary electron beam and the atoms on the surface of the specimen, a number of signals are produced. Secondary electrons, which are low-energy electrons emitted from the surface of the specimen, are very surface-sensitive. Backscattered electrons,

which are high-energy elastically scattered electrons by the atomic nuclei, produce composition contrasts because of their dependence on the atomic number of the elements. In addition, the interaction between the incident electron beam and inner-shell electrons of the sample atoms leads to the emission of characteristic X-rays, which can be analyzed for elemental composition when coupled with an energy-dispersive X-ray detector. The electron beam scans the surface point by point in a controlled raster pattern. The detected signals are synchronized with the beam position and processed to construct a high-resolution two-dimensional image of the sample surface. The contrast and information content of the image depend on the type of signal detected [19].

2.3.3 Information obtained from FE-SEM

FE-SEM delivers detailed information on the material's surface and microstructural properties that include:

- **Surface morphology** High-resolution micrographs reveal about particle size, particle shape, surface texture, porosity and degree of agglomeration.
- **Microstructural Features::** Identification of nanoscale structure details such as layered structures, grain boundaries, cracks, voids and defects.
- **High-magnification imaging:** Imaging from micrometer to nanometer scale with high depth of field and excellent spatial resolution.
- **Elemental composition:** When coupled with Energy Dispersive X-ray (EDX) analysis it can provide information about the elemental composition and distribution.

2.4 Transmission Electron Microscopy

2.4.1 Principle

Transmission Electron Microscopy (TEM) is a high-resolution characterization technique used to study the internal structure of materials at the nanometre and atomic scales. The technique is based on the transmission of a high-energy electron beam

through an ultra-thin specimen. As the electrons pass through the sample, they interact with its atomic structure and undergo scattering to different extents depending on the local composition and structure of the material [20].

Although electrons are particles, they also exhibit wave-like characteristics. The wavelength of electrons is inversely proportional to their kinetic energy, hence those accelerated to high voltages have extremely small wavelengths. These small wavelengths make it possible for TEM to have significantly greater resolution than optical microscopy. Depending on how the beam of electrons is transmitted through the thin sample, interactions in the form of elastic and inelastic scattering, diffraction, and transmission without interaction occur to the electrons. Image contrast in TEM images is created based on variations in either thickness, density, and/or atomic number caused by how the sample scatters the incoming electrons [21].

2.4.2 Instrumentation/ Construction and working

A conventional transmission electron microscope consists of several key parts: an electron generation unit, an electromagnetic lens system, a specimen supporting system, a vacuum system, and an image detection and control system as illustrated in Figure 2.6. The electron generation unit uses either a thermionic or field-emission gun that provides high-energy electrons. These electrons are transported through the microscope column using electromagnetic lenses. In this process, the objective lens is the one that provides high resolution [22].

The specimen mounting system enables the mounting of electron-translucent specimens. These specimens are usually mounted as ultra-thin films. In most instances, the specimen matter is suspended in a solvent like ethanol and then placed on a carbon-covered copper grid to facilitate the passage of electrons. The whole microscope column is maintained under ultra-high vacuum conditions to ensure that the electron beams are not scattered or absorbed by the gases that make up the atmosphere. The overall operation of the microscope, including beam alignment, focusing, image acquisition, and data processing, is controlled through a computer-based imaging and control unit [21].

Within the Transmission Electron Microscopy analysis, a highly energetic electron beam is initially produced by the electron gun, which is accelerated at high voltage levels, typically in the range of 10 keV to 100 keV. The accelerated electron beam is subsequently condensed and focused on a fine electron beam using an electromagnetic condenser lens. The focused electron beam is projected on to the ultra-thin specimen, which is positioned on the sample holder. As the electron beam passes through the specimen, it interacts with the atomic structure of the specimen. Based on the local thickness, composition, and crystallinity, the electrons experience both elastic and inelastic scattering. A certain fraction of the electron beam manages to pass through the specimen with negligible interaction, while others get scattered with varying degrees. The fraction of the electron beam passing through and being scattered carries information with regard to the atomic structure of the specimen.

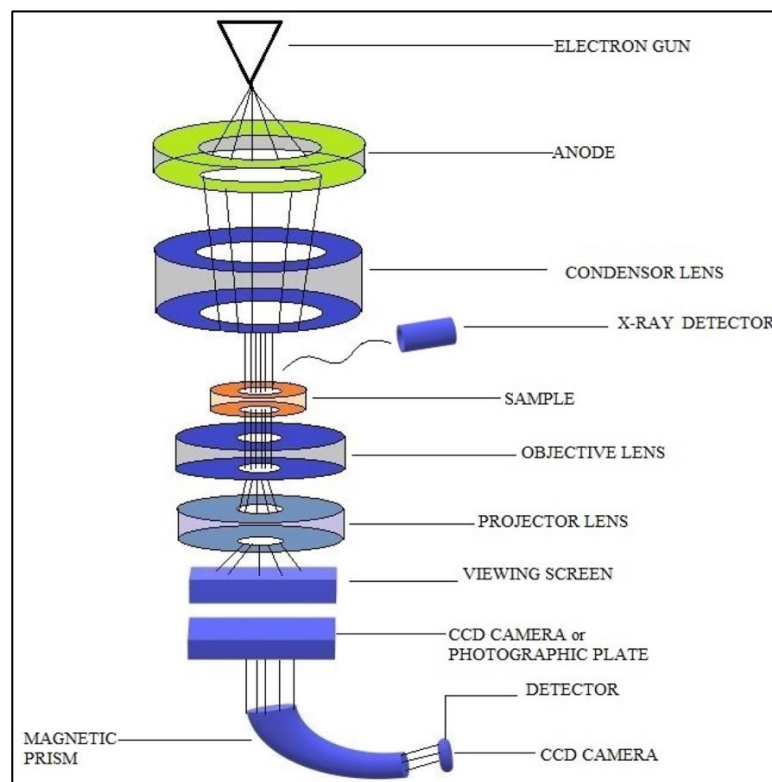


Figure 2.6. Schematic diagram of a Transmission Electron Microscope (TEM) illustrating the electron gun, condenser lenses, specimen stage, objective lens, intermediate and projector lenses and the imaging system used to generate high-resolution images of materials. Reproduced with permission from Ref. [42].

The electrons emerging from the specimen are collected by the objective lens, which forms a magnified image or diffraction pattern. This image is further enlarged by the projector lens system and projected onto a fluorescent viewing screen or recorded digitally using a CCD camera. The variation in electron scattering within different regions of the specimen results in contrast in the final image. By adjusting the operating conditions of the microscope, TEM can be used either to obtain high-resolution images of the internal morphology or to record electron diffraction patterns for crystallographic analysis [23,24].

2.4.3 Information obtained from TEM analysis

Some of the information obtained from TEM analysis are as follows:

- **Morphology and Size:** TEM allows analyses to be conducted on the internal structure of materials, such as layers, nanosheets, nanoparticles, or core shell or composite morphology.
- **Crystallinity:** This allows characterization of the crystalline and amorphous parts of the sample. High-resolution TEM micrographs can reveal lattice fringes, indicating that the material is indeed crystalline.
- **Interplanar Spacing:** Lattice fringe images can be used to measure interplanar distances (d-values), which assist in identifying crystal planes and phases.
- **Crystal structure & phase analysis:** Selected Area Electron Diffraction (SAED) patterns are related to the structure of crystals, symmetry, and phase composition of the material.
- **Elemental Composition (with EDS):** When paired with energy dispersive X-ray spectroscopy, the TEM can be used for qualitative and quantitative analysis of the elemental composition and distribution at a nanoscale level.

2.5 Fourier Transform Infrared Spectroscopy

2.5.1 Principle

Fourier transform infrared (FTIR) spectroscopy is one of the most powerful and widely employed vibrational spectroscopic techniques for the qualitative and quantitative characterization of materials. The technique is based on the interaction of infrared radiation (IR) with matter, which includes molecular vibrations associated with changes in the dipole moment of chemical bonds. Most covalently bonded molecules exhibit characteristic vibrational frequencies and FTIR spectroscopy provides a unique fingerprint of chemical composition, functional groups and bonding environments. FTIR spectroscopy is routinely used across a broad range of scientific disciplines, including chemistry, materials science, chemical engineering, catalysis, polymer science, nanotechnology, environmental science and biomedical research. Its popularity stems from several advantages, such as minimal sample preparation, non-destructive analysis, high sensitivity to chemical bonding and the ability to analyse solids, liquids, gases and surface species using different experimental configurations. In materials research, FTIR spectroscopy plays a crucial role in identifying groups, confirming chemical modifications, monitoring surface reactions and studying intermolecular interactions. The technique is particularly valuable for investigating carbon based materials, metal oxides, composites, polymers and nanostructured systems, where subtle changes in bonding and surface chemistry strongly influence materials properties [24].

The fundamental principle of FTIR spectroscopy is based on the absorption of infrared radiation by molecules, leading to transition between different vibrational energy levels. Unlike ultraviolet or X-ray radiation, infrared radiation does not possess sufficient energy to induce electronic transitions. Instead, it excites vibrational and in some cases, rotational motions of atoms within a molecule. For a vibrational mode to be infrared active, it must be associated with a change in the dipole moment of the molecule. As a result, homonuclear diatomic molecules such as N₂, O₂ and H₂ do not exhibit IR absorption, whereas most covalently bonded polyatomic molecules display

characteristic IR spectra. The position of an absorption band is primarily determined by the vibrational frequency of a bond, while the intensity of the band depends on the magnitude of the dipole moment change during vibration.

The infrared region of the electromagnetic spectrum is conventionally divided into three regions: the near-infrared (NIR) region ($\sim 14,000\text{--}4,000\text{ cm}^{-1}$), the mid-infrared (MIR) region; $\sim 4,000\text{--}400\text{ cm}^{-1}$, and the far-infrared (FIR) region $<400\text{ cm}^{-1}$. The mid-infrared region is the most commonly used for FTIR-analysis, as it contains the fundamental vibrational modes of most functional groups and provides rich chemical information. The molecular vibrations observed in FTIR spectroscopy are broadly classified into stretching and bending modes as shown in Figure 2.7. Stretching vibrations involve changes in bond length along the bond axis and can be further categorized as symmetric or asymmetric stretching. Bending vibrations involve changes in bond angle without significant alteration of bond length and include rocking, scissoring, wagging and twisting motions. The vibrational frequency of a bond can be approximated using Hooke's law, which treats the bond as a harmonic oscillator. According to this model, the vibrational frequency depends on the bond strength (force constant) and the reduced mass of the bonded atoms and can be expressed as follows

$$F = -kx \quad (2.4)$$

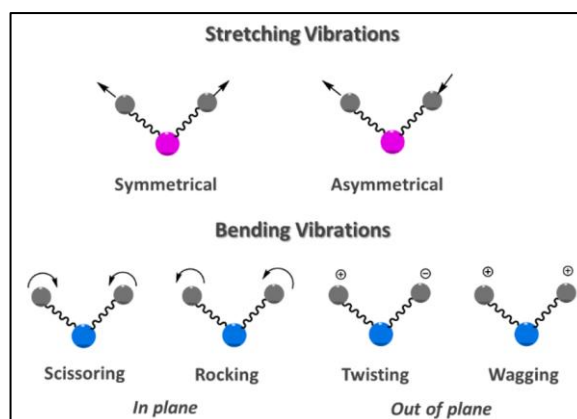


Figure 2.7. Schematic representation of stretching and bending vibrational modes in molecules. Reproduced with permission from Ref. [26].

Consequently, stronger bonds and lighter atoms give rise to higher vibrational frequencies, while heavier atoms and weaker bonds vibrate at lower frequencies [25].

2.5.2 Instrumentations/Construction and Working

A FTIR spectrometer consists of four essential components: an infrared radiation source, an interferometer, a sample compartment with appropriate accessories and a detector coupled with a data processing system. A schematic diagram of a typical FTIR instrument is shown in Figure 2.8. The IR source provides a broad, continuous spectrum of infrared radiation. Commonly used sources include silicon carbide and Nerst glowers, which emit stable IR radiation over a wide wavelength range. The stability and intensity of the source are critical for obtaining high quality spectra with good signal to noise ratios. The defining feature of FTIR spectroscopy is the use of an interferometer instead of a monochromator. The most widely employed configuration is the Michelson interferometer, which consists of beam splitter, a fixed mirror and a recombined to produce an interference pattern that is known as an interferogram.

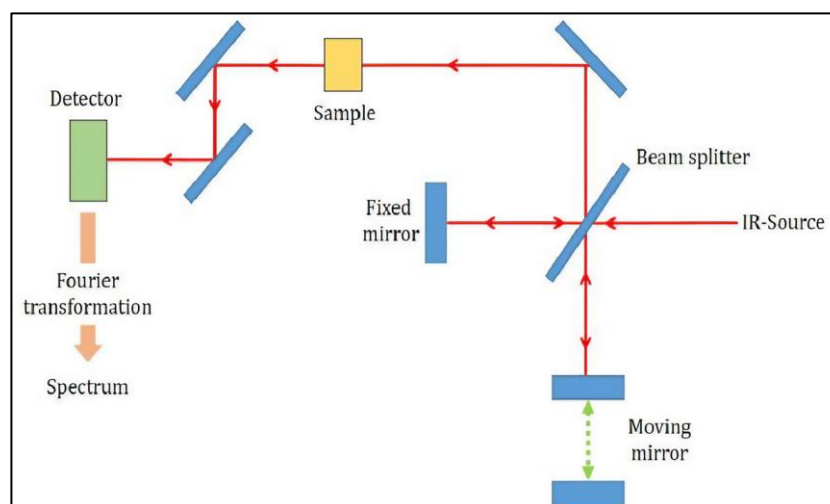


Figure 2.8. Schematic diagram of an FTIR spectrometer illustrating the infrared source, beam splitting unit with fixed and moving mirrors, sample compartment, detector and computer system used to convert the recorded interferogram into an infrared spectrum. Reproduced with permission from Ref. [27].

As the moving mirror changes position, the optical path difference between the two beams varies, resulting in constructive and destructive interference for different

wavelengths. The interferogram contains information from all wavelengths simultaneously and is mathematically transformed into a conventional IR spectrum using a Fourier transform algorithm. FTIR spectroscopy offers multiple experimental configurations to accommodate different types of samples: Transmission FTIR, where IR radiation passes directly through a thin sample or KBr pellet. Attenuated Total Reflection (ATR), which utilizes an evanescent wave generated at the interface between an internal reflection element and the sample. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), suitable for powders and highly scattering materials. Reflection–Absorption Infrared Spectroscopy (RAIRS), used primarily for thin films and surface studies. Each configuration offers distinct advantages depending on sample morphology, thickness, and chemical composition.

Detectors convert the IR radiation into an electrical signal. Common detectors include deuterated triglycine sulfate (DTGS) detectors and mercury cadmium telluride (MCT) detectors. The choice of detector influences sensitivity, response time, and spectral resolution. The acquired interferogram is processed using Fourier transformation to generate the final absorbance or transmittance spectrum. During FTIR analysis, infrared radiation emitted from the source is first modulated by the interferometer due to the movement of the mirror, producing an interferogram that contains information from all IR frequencies simultaneously. This modulated beam then interacts with the sample placed in the sample compartment. As the IR radiation passes through the sample, specific vibrational frequencies corresponding to the molecular bonds are absorbed, while the remaining frequencies are transmitted. The detector records the intensity variations of the transmitted radiation as a function of optical path difference, generating the interferogram in the time domain. The recorded interferogram is mathematically transformed using a Fourier transform algorithm to convert it into a conventional frequency-domain spectrum. The resulting FTIR spectrum typically spans the wavenumber range of 400–4000 cm^{-1} and displays characteristic absorption bands corresponding to various functional groups and bonding environments present in the material. Owing to the simultaneous data acquisition and internal calibration, FTIR measurements are rapid, highly reproducible, and suitable for routine as well as advanced material characterization [24].

2.5.3 Information obtained from FTIR analysis

FTIR spectroscopy provides comprehensive qualitative information about the chemical nature of materials, as summarized below:

- **Identification of functional groups:** FTIR spectroscopy enables the identification of various functional group such as –OH, –NH, C–H, C=O, C–O, C–N, and metal–oxygen (M–O) bonds through their characteristic absorption bands.
- **Determination of vibrational modes:** FTIR analysis provides detailed information about vibrational modes, including stretching and bending vibrations, which help in understanding molecular geometry and bonding characteristics.
- **Evaluation of material purity and compositional uniformity:** In case of polymers, nanocomposites, and hybrid materials, FTIR spectroscopy can be used to evaluate material purity and compositional uniformity.

2.6 Ultraviolet -Visible Spectroscopy

2.6.1 Principle

Ultraviolet visible (UV-Vis) spectroscopy is one of the most fundamental and extensively utilized spectroscopic techniques for the characterization of materials due to its simplicity, rapid analysis, non-destructive nature and broad applicability. The technique is based on the interaction of electromagnetic radiation in the ultraviolet and visible regions with matter, leading to electronic excitation that gives characteristics absorption bands. Typically, UV-vis spectroscopy operates in the wavelength range of approximately 200-800 nm, although many modern instruments are capable of extending measurements into the near-infrared region. The widespread adoption of UV-Vis spectroscopy across Chemistry, materials science, pharmaceuticals and chemical engineering arises from its ability to provide both qualitative and quantitative insights into electronic structure of a wide variety of materials. It is particularly valuable for studying organic molecules, coordination complexes, conjugated

systems, nanomaterials and semiconductor materials. As a result UV-visible spectroscopy is the most common technique employed to monitor reaction kinetics, investigating molecular interactions, characterize nanoparticles and estimate optical band gaps of semiconducting materials [28].

The working principle of UV-Vis spectroscopy is based on the absorption of ultraviolet or visible radiation by atoms or molecules, resulting in electronic excitation. When electromagnetic radiation of suitable energy interacts with a material, electrons initially present in lower-energy molecular orbitals may absorb energy and transition to higher energy excited states. Absorption occurs only when the energy of the incident radiation exactly matches the energy difference between the ground and excited electronic states. The electronic transitions responsible for UV-Vis absorption generally involve electrons associated with σ (bonding), π (bonding) or n (non-bonding) orbitals. The various transition possible are shown in Figure 2.9. Upon absorption of radiation, these electrons may be promoted to corresponding antibonding orbitals such as σ^* or π^* . Among the various possible transitions, $\sigma \rightarrow \sigma^*$ transitions require very high energy and typically occur in the far-ultraviolet region, whereas $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions fall within the experimentally accessible UV-visible range. Consequently, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ transitions are most commonly observed in UV-vis spectra of organic and conjugated systems [29,30].

The functional groups responsible for absorption in the UV-visible region are referred to as chromophores, while substituent groups that do not absorb strongly themselves but influences the position and intensity of absorption bands are known as auxochromes. The presence of auxochromes can modify the electronic environment of chromophores, resulting in shifts in absorption maxima and changes in band intensity. Variations in conjugation length, molecular planarity, solvent polarity and intermolecular interactions can result in bathochromic (red) or hypsochromic (blue) shifts, as well as hyperchromic or hypochromic effects in absorption intensity. Quantitatively, UV-vis analysis is governed by the Beer-Lambert law, which establishes a linear relationship between absorbance and concentration as given in Equation 2.5.

$$A = \epsilon bc \quad (2.5)$$

Where A is the absorbance, ϵ is the molar absorptivity, b is the optical path length, and c is the concentration of the absorbing species. This relationship forms the theoretical foundation for concentration determination, calibration curve construction, and kinetic studies using UV-Vis spectroscopy, provided that measurements are carried out within the linear absorbance range [28].

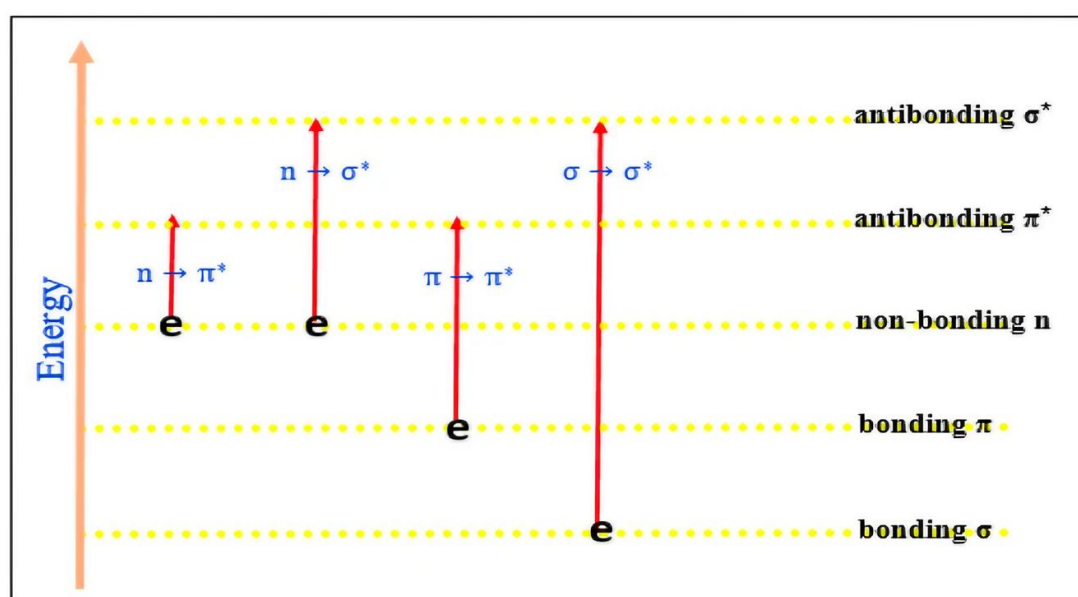
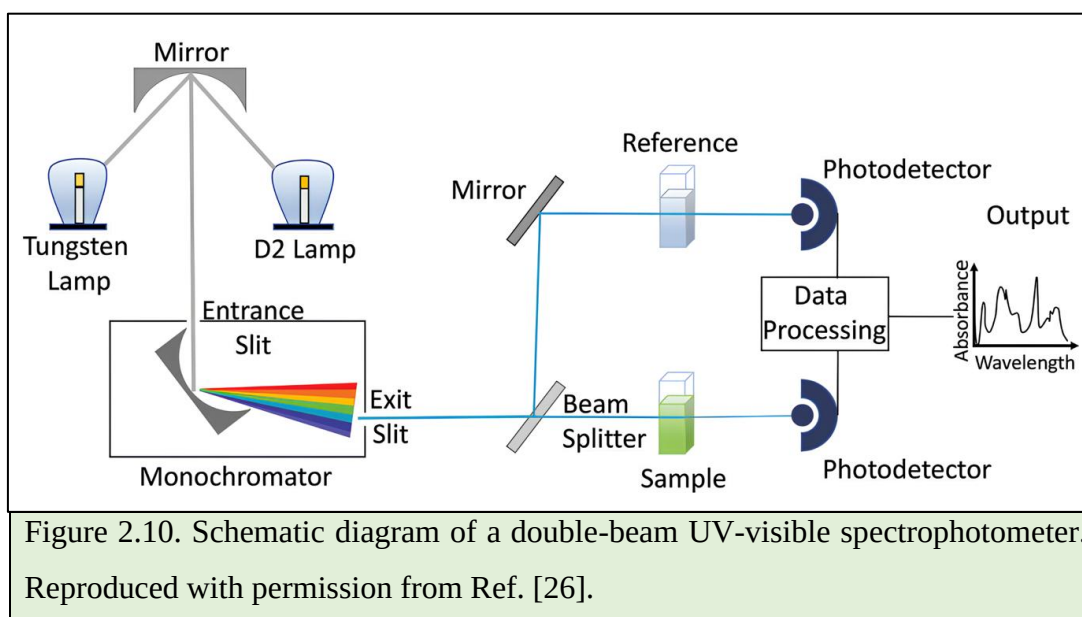


Figure 2.9. Schematic energy level diagram illustrating electronic transitions in molecules upon absorption of UV-visible radiation. Reproduced with permission from Ref. [31].

2.6.2 Instrumentation/Construction and working

A UV-Vis spectrophotometer consists of several essential components that operate together to generate accurate and reproducible absorption spectra. A schematic diagram of UV-visible spectrometer is shown in Figure 2.10. The radiation source must provide a stable and continuous output over the required wavelength range. For ultraviolet measurements, deuterium lamps are widely used due to their continuous emission in the UV region. For visible region analysis, tungsten or tungsten halogen lamps are commonly employed. Some advanced instruments utilize xenon lamps,

which offer a broad emission spectrum covering both ultraviolet and visible regions. The monochromator is responsible for isolating a narrow wavelength band from the polychromatic radiation emitted by the light source. It typically consists of an entrance slit, collimating optics, a dispersing element (prism or diffraction grating), focusing optics and an exit slit. Diffraction gratings are generally preferred over prisms because they provide better wavelengths resolution and more uniform dispersion across the spectral range. Samples are placed in optically transparent cuvettes that allow radiation to pass through with minimal absorption by the container. Quartz or fused silica cuvettes are essential for ultraviolet measurements, as conventional glass absorbs strongly below 350 nm. For measurements restricted to the visible region, glass cuvettes may also be employed [28].



The detector converts transmitted or reflected radiation into an electrical signal proportional to light intensity. Photomultiplier tubes and photodiode array detectors are commonly used due to their high sensitivity, rapid response time and low noise characteristics. The detected signal is processed electronically and displayed as absorbance or transmittance as a function of wavelength.

During a UV-Vis measurement. Radiation emitted from the light source is directed into the monochromator, where a specific wavelength is selected. The monochromatic beam then passes through the sample, where partial absorption occurs depending on

the electronic structure and concentration of the absorbing species. The remaining transmitted radiation reaches the detector, which measures the intensity relative to the incident or reference beam.

In single beam instruments, measurements of the blank and sample are carried out sequentially, whereas in double beam instruments the radiation is divided into sample and reference beams, enabling real-time correction for instrumental drift and source fluctuations. The resulting spectrum is recorded as absorbance versus wavelength, with absorption maxima corresponding to specific electronic transitions within the material. An important practical consideration in UV-Vis spectroscopy is the choice of solvent, as the solvent itself should not significantly absorb radiation in the wavelength region of interest. Ideally, the solvent must be optically transparent over the selected spectral range so that the measured absorption originates solely from the analyte. Water and lower alcohols such as ethanol are among the most commonly used solvents in UV-vis spectroscopy because of their high transparency in the visible region and minimal absorption in much of the ultraviolet range [28–31].

2.6.3 Information obtained from UV–Visible Spectroscopy

UV–Visible spectroscopy provides the following important information:

- **Identification of electronic transitions:** UV-Vis spectroscopy enables the identification of electronic transitions such as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, which help in understanding the electronic structure of molecules and materials.
- **Determination of optical absorption characteristics:** UV-Vis analysis allows the determination of optical absorption characteristics, including absorption maxima (λ_{max}), which are indicative of specific chemical functionalities or conjugation length.
- **Estimation of optical band gap:** The optical band gap of semiconductors and nanomaterials, can be estimated using Tauc plots derived from UV–Vis absorption data.

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- **Analysis of concentration and dispersion:** UV-Vis spectroscopy facilitates the analysis of concentration for liquid samples and colloidal suspensions, based on absorbance intensity and Beer–Lambert law.

2.7 Raman Spectroscopy

2.7.1 Principle

Raman spectroscopy is a powerful vibrational spectroscopic technique widely employed for molecular characterization based on inelastic light scattering. The phenomenon underlying this technique, known as the Raman effect, was discovered in 1928 by the Indian physicist C.V. Raman, along with his collaborator K.S. Krishnan. During their experiments on the interaction of monochromatic light with transparent materials, they observed that when monochromatic light passes through a transparent material, most of the scattered light has the same wavelength as the incident light, but a very small portion shows a change in wavelength. This frequency shift, which could not be explained by classical elastic scattering, was attributed to energy exchange between incident photons and molecular vibrational modes. The discovery was rapidly recognized as a major scientific breakthrough and earned C.V. Raman the Nobel Prize in Physics in 1930 [32].

The Raman effect arises due to inelastic scattering of photons, where in incident light interacts with molecular vibrations, resulting in scattered photons with either lower or higher energies compared to the excitation source. This frequency shift is characteristic of the molecular structure and bonding environment of the scattering species. This unique features allows Raman spectra to serve as molecular fingerprints, enabling reliable identification and structural analysis of materials.

When monochromatic radiation interacts with matter, scattering of light occurs. This scattering process can be broadly classified into elastic and inelastic scattering. In elastic scattering, also known as Rayleigh scattering, the scattered photons has the same energy and wavelength as the incident light. This type of scattering does not provide information about molecular vibrations. In contrast, inelastic scattering

involves a change in energy between the incident photon and the molecule. This type of scattering is known as Raman scattering and forms the basis of Raman spectroscopy. During Raman scattering, the incident photon temporarily excites the molecule to a virtual energy states. The molecule then relaxes back to a different vibrational energy level, resulting in scattered light with a shifted frequency. The difference between the frequencies of the incident and scattered light corresponds to the vibrational energy of the molecule. There are two types of Raman scattering: Stokes and Anti-Stokes scattering. Stokes scattering occurs when the molecule gains energy from the incident photon. As a result, the scattered photon has lower energy and lower frequency than the incident light. Stokes lines are stronger and are commonly used in Raman analysis. Anti-Stokes scattering occurs when the molecules lose energy to the incident photon. In this case, the scattered photon possesses higher energy and therefore higher frequency compared to the incident radiation. However, since at room temperature most molecules remain in their ground vibrational state, the population of excited vibrational levels is relatively low. Anti-Stokes lines are generally weaker in intensity than Stokes lines and are less commonly used for routine analysis. Figure 2.11 represents all the electronic and vibrational transitions involved in Raman spectroscopy.

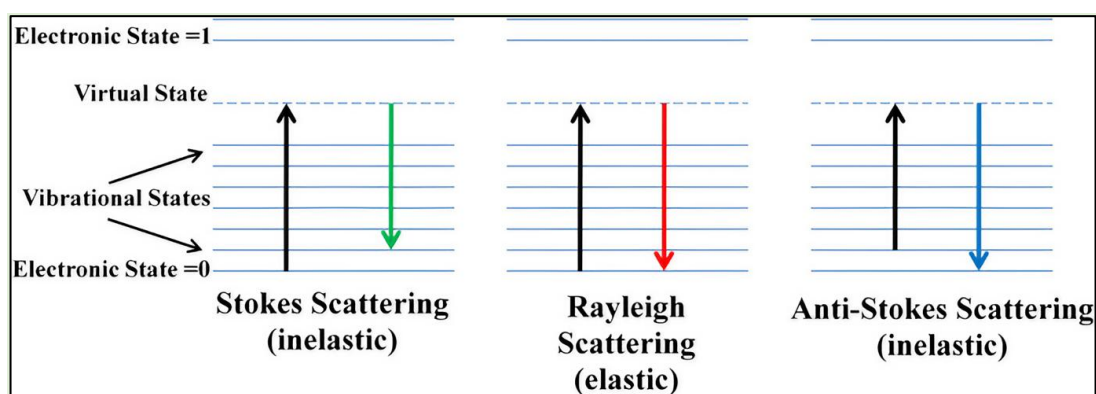


Figure 2.11. Jablonski energy level diagram depicting the electronic and vibrational transitions involved in Raman spectroscopy, highlighting Stokes Raman scattering, Rayleigh scattering and Anti-Stokes Raman scattering processes. Reproduced with permission from Ref. [33].

The energy difference between the incident and scattered photons corresponds precisely to the vibrational energy levels of the molecule. Therefore, the Raman shift, usually expressed in wavenumbers (cm^{-1}), provides direct insight into molecular vibrations bonding characteristics and symmetry [34]. For a vibrational mode to be Raman active, it must involve a change in molecular polarizability during vibration. Polarizability refers to the ease with which the electron cloud of a molecule can be distorted by an external electric field. Vibrations that cause significant redistribution of electron density tend to produce strong Raman signals.

Typically, symmetrical vibrations and non-polar bonds exhibit higher Raman activity. Functional groups such as $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}-\text{S}$, $\text{S}-\text{S}$ and $\text{C}-\text{X}$ (where X = halogens) displays strong Raman scattering due to pronounced polarizability changes. This selection rule makes Raman spectroscopy complementary to Infrared spectroscopy, which is governed by changes in dipole moment. The vibrational information obtained from Raman spectroscopy allows both qualitative and quantitative analysis of materials. Since Raman spectra are highly sensitive to molecular structure, symmetry and chemical environment, even subtle structural vibrations can be detected. Moreover, Raman spectroscopy requires minimal sample preparation, is largely non-destructive, and can be applied to solids, liquids and gases. These attributes have contributed significantly to its widespread adoption and continued technological advancement [35–37].

2.7.2 Instrumentation/Construction and working

A typical Raman spectrometer consists of four essential components: the excitation source, sample illumination system, wavelength selection unit, and detector. Each component plays a crucial role in obtaining high quality Raman spectra. The excitation source forms the foundation of Raman spectroscopy. It provides intense, monochromatic and coherent radiation that interacts with the molecular vibrations of the sample to produce Raman scattering. In modern Raman instruments lasers are preferred over conventional light sources because they provide narrow spectral linewidth, they offer high intensity and they ensure stable and coherent illumination.

Common laser sources include argon ion lasers, helium-neon lasers, diode lasers etc. The selection of laser wavelength is highly important. Since Raman scattering intensity varies inversely with the fourth power of wavelength, shorter wavelengths generally produce strong Raman signals. However, shorter wavelengths may induce fluorescence in certain samples, which can interfere with Raman measurements. Therefore, near infrared excitation sources are often used for fluorescence prone materials. Laser stability and power directly influence the reproducibility and quality of the recorded Raman spectrum.

Once the coherent laser radiation is generated, it must be precisely directed onto the sample. This is accomplished using a series of optical components, including mirrors, beam splitters, lenses, microscope objectives. These elements guide the laser beam toward the sample and focus it onto a small region. In micro Raman systems microscope objectives with high magnification are used to concentrate the beam to a micrometre scale spot. Efficient focusing enhances photon-sample interaction and increases the probability of Raman scattering. Proper optical alignment is essential to ensure maximum collection efficiency and signal strength. On the other hand the sample stage provides mechanical stability and proper positioning of the sample during analysis. Raman spectroscopy can be applied to a wide range of sample types, including: solids (powders, pellets, thin films), liquids in cuvettes, biological tissues, polymers and nanomaterials. When the laser interacts with the sample, scattered radiation is emitted in all directions. The collection optics gather this scattered light and direct it into the spectrometer. Most Raman instruments use a backscattering geometry, where the same objective lens used for excitation also collects the scattered radiation.

This design improves efficiency and compactness of the system. The collected light contains not only weak Raman scattered radiation but also highly intense Rayleigh scattered light. Since Rayleigh scattering is several orders of magnitude stronger than Raman scattering, it must be removed before spectral analysis. This is achieved using specialized optical filters, such as edge filters, notch filters and holographic filters. These filters selectively block radiation at the laser excitation wavelength while

allowing Raman shifted light to pass through. Proper filtering is essential because without suppression of Rayleigh scattering, the weak Raman signal would be invisible by the intense elastic scattering [35]. After filtering, the remaining scattered light enters the monochromator or spectrometer. This component disperses the Raman light according to its wavelength or Raman shift. A typical monochromator includes: entrance slit, diffraction grating, focusing optics. The diffraction grating separates the Raman shifted light into its constituent wavelengths so that each Raman peak can be resolved. The dispersion and resolution of the grating determine the spectral clarity and accuracy of the Raman data. The dispersed Raman light is detected by a sensitive photodetector. Modern Raman systems predominantly use charge coupled devices (CCDs) due to their high sensitivity wide spectral range and efficiency in detecting weak light signals.

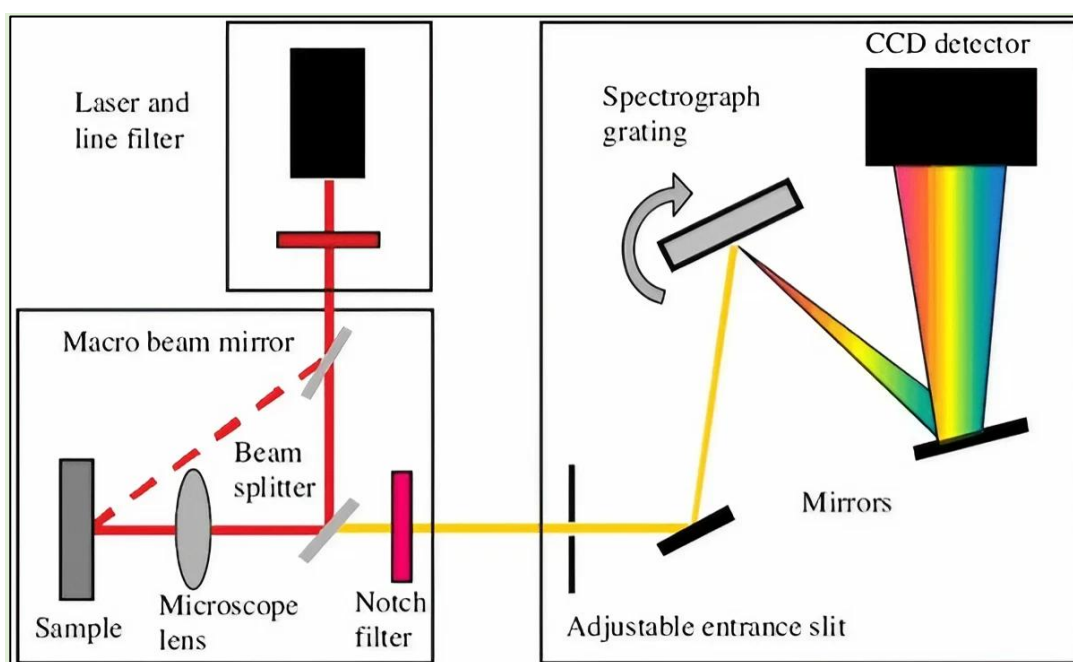


Figure 2.12. Schematic diagram of a Raman spectrometer showing the major components and optical pathway. Reproduced with permission from Ref. [38] .

The electrical signal from the detector is processed by a computer system with dedicated software. The software perform the following: baseline correction, spectral calibration, peak position identification and quantitative intensity analysis. The output

is presented as a graph of intensity versus Raman shift (cm^{-1}), which provides detailed vibrational information about the sample [36].

2.7.3 Information obtained from Raman Spectroscopy

The following information can be obtained from Raman spectroscopic analysis:

- **Molecular Vibrational Information:** Raman spectroscopy provides detailed insight into the vibrational characteristics of materials, which are directly related to their structural and chemical properties.
- **Molecular structure and bonding:** The technique gives insight into the type of chemical bonds present in a material. It helps in identifying bond strength, bond symmetry and functional groups. Variation in peak position and intensity reflect changes in the bonding environment.
- **Phase Identification:** Different crystalline phases exhibit unique Raman signatures. Therefore, Raman spectroscopy is useful for identifying and differentiating between various structural phases or polymorphs of a material.
- **Stress and Strain Analysis:** Mechanical stress or strain in a material often causes measurable shifts in Raman peak positions.

2.8 Electrochemical characterization

All electrochemical measurements were carried out using a Metrohm Autolab PGSTAT204 electrochemical workstation (Metrohm Autolab B.V., The Netherlands). The instrument (Figure 2.13) is equipped with a high-performance potentiostat/galvanostat and controlled through NOVA 2.1.8 software for data acquisition and analysis. The workstation supports both three-electrode and two-electrode measurement configurations. In the three-electrode configuration, a conventional setup consisting of a working electrode (prepared active material coated on current collector), a reference electrode (Ag/AgCl or Hg/HgO, depending on the electrolyte), and a platinum wire (or graphite rod) counter electrode was employed

(Figure 2.14 (a)). This configuration was used to investigate the intrinsic electrochemical behavior of the electrode material.



Figure 2.13. PGSTAT 204 and Nova 2.1.8 loaded on computer.

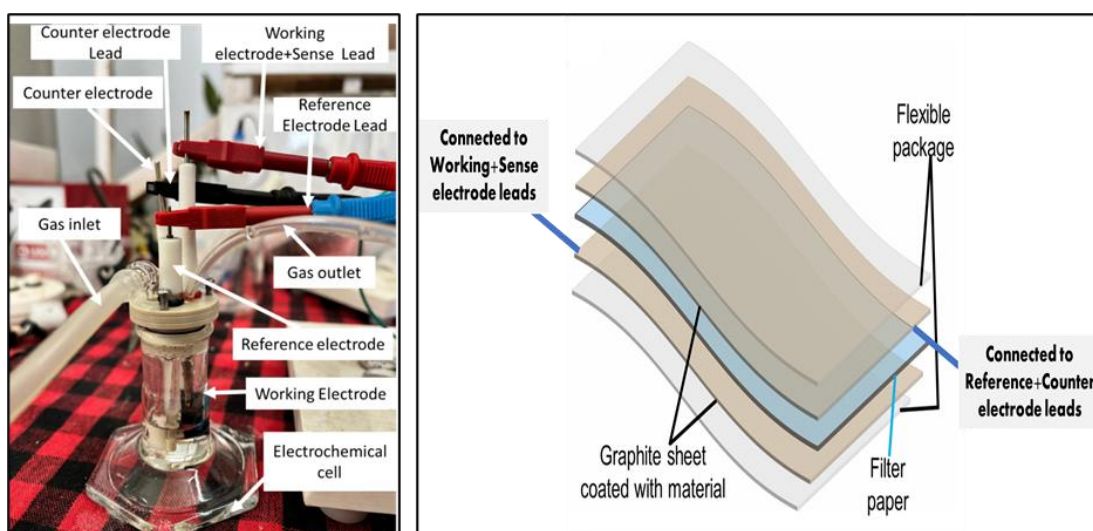


Figure 2.14. (a) Three-electrode configuration depicting the WE, RE, and CE connected to the Metrohm Autolab PGSTAT204 potentiostat. (b) Schematic representation of the two-electrode configuration used for supercapacitor device testing.

For practical device-level evaluation, a two-electrode configuration was used, where the assembled symmetric supercapacitor device served as the electrochemical cell (Figure 2.14 (b)). This setup provides a more practical evaluation of the electrochemical performance under actual operating conditions. Electrochemical characterization techniques including cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed using this workstation.

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Chapter 3



DFT study on the structural,
optical and electronic
properties of platinum group
doped graphene

CHAPTER 3

DFT study on the structural, optical and electronic properties of platinum group doped graphene

3.1 Introduction⁺

Since the past few decades, there has been a surge in the use and application of nanomaterials across the globe [1–7]. Their fascinating properties make them extensively employable in numerous fields of science and technology such as drug delivery systems, tissue engineering, treatment of cardiovascular and neurological diseases, paints, cleaning products, cosmetics, filtration, sensors etc. [8–13]. Among the various classes of nanomaterials, carbon-based nanomaterials such as carbon nano tubes (CNTs), activated carbon (AC), fullerenes etc. have attracted wide attention due to their efficiency and diverse applications [14–23]. In recent times, another allotrope of carbon, graphene has captured the fascination of the scientific community because of its exceptional set of properties [24–31]. Graphene is a 2D array of sp^2 hybridized carbon atoms arranged in a hexagonal honeycomb lattice to form a flat monolayer of carbon atoms [24,32,33]. Geim and Novoselov were the first to isolate it in 2004 [34] and it is the basic building block of other graphitic materials of all other dimensionalities such as fullerenes, nanotubes, graphite. The graphene sheets can be wrapped up to form 0D fullerenes, rolled to form 1D nanotubes or stacked on top of each other to form the 3D graphite. In other words, it can be considered as the “Mother of all graphitic forms” [24]. It exhibits unique properties such as high specific surface area, high conductivity [24], excellent optical, electronic [29], thermal and mechanical [30,31] properties etc. These inimitable and alluring properties of graphene makes it a potent material candidate in a wide array of fields such as catalysis [35,36], sensors [37,38], energy storage [39–41], water purification [42,43], optoelectronics [44] as well as in many other applications [24,34,45–47]. Despite these favourable properties, there are many challenges that restrict the use of graphene in manufacturing devices [48], thereby causing immense need to tailor the properties of graphene as per the needs and requirements for its use in diverse applications.

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In this regard a substantial amount of work has been done to fine tune graphene's properties [49–55]. Recently, the method of doping has drawn much attention as it is one of the simplest and effective ways to alter and modulate the properties of graphene, which can be achieved by regulating the degree of doping and/or doping with different hetero atoms [56]. It is found that the electronic properties of graphene like charge distribution, density of states, energy levels etc. change considerably when doped with heteroatoms such as N, B, O etc. [35,50,53,56–59], possibly due to the electronegativity difference between carbon atom and the dopants. Although, doping with various heteroatoms have been extensively studied, there are limited reports about doping with platinum group elements (PGE) and its effects on the structural, optical and electronic properties of graphene [60–64].

PGE consists of ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt), and has a number of desirable properties such as high mechanical strength, ductility, good electrical properties. The use of PGE such as Pt, Pd to graphene/graphene support materials has demonstrated enhanced catalytic performance such as boosted oxygen reduction[65–67], methanol oxidation [68,69], improved durability of catalyst etc. [60,65]. Recently, Yang et al. showed that the catalytic reduction of NO with NH_3 at low temperature can be amplified by doping graphene catalysts with PGE (Pt, Pd, Ru and Rh) and concluded that PGE have promoting effects in the whole catalytic process [70]. Chen et al. concluded that inserting Pt on nitrogen doped graphene tubes boosted stability and exhibited exceptional catalytic activity [65]. In addition, PGE doped graphene would also be a compelling candidate for use in various fields such as electronics, energy storage, solar cells etc.[71,72].

Therefore, in this study, we present a density functional theory (DFT) study of the structural, optical and electronic properties of pristine graphene and investigate the modification in these properties when pristine graphene is doped with PGE in order to improve the scope of this material for future applications.

3.2 Computational details

All density functional theory (DFT) calculations were performed using the Gaussian 09 software package [73] using B3PW91 functional [74] and Los Alamos National Laboratory 2 double-Zeta (LANL2DZ) [75–77] basis set. B3PW91 functional employs Becke -3 parameters [78] with PW91 correlation functional and produces consistently good results for large systems, especially systems containing transition metals [79–81]. B3PW91 possesses precise free-electron gas limiting behavior which consequently results in production of fairly accurate results [82]. LANL2DZ basis set is a commonly used effective core potential (ECP) basis which incorporates the relativistic effects for the heavy transition atoms/metals [83,84]. It has been reported that DFT functionals when coupled with LANL2DZ basis set predicted results closer to experimental values for systems containing transition metals/atoms [61,63,64,84–86]. Therefore, in the present study, B3PW91/LANL2DZ level of theory was employed, since our calculations involves transition metals. The molecules were optimized to their lowest energy states, coupled with frequency calculations without any symmetry constraints. The absence of any imaginary frequency confirmed that the systems attained their lowest energy states.

Quantum calculations involving graphene typically employ graphene cell periodic calculations or molecular systems as models. In particular, numerous studies have shown that graphene can be modelled as a coronene ($C_{24}H_{12}$) molecule[87–93] and is considered a good prototype in the absence of periodic calculations [94,95]. Various studies make use of this approach [96–99]. Therefore, in the present study, the molecular system i.e., graphene, is modelled as a coronene molecule containing 24 Carbon atoms, which are saturated at the edges by 12 hydrogen atoms to avoid dangling of bonds. Figure 3.1(a) presents a coronene molecule which is used as a model for graphene in which the edges are saturated to replicate continuity of the surface [61]. Various reports suggest that defects in graphene also play a vital role in deposition of any kind of heteroatom [85]. The vacancies formed are found to exhibit strong interactions with doped metals as established in several theoretical studies [100–102]. Moreover, when PGE such as Pt, Pd is deposited over monovacant site of graphene, the metals bind with the surrounding carbon atoms, thereby getting incorporated in graphene [85]. Various reports in literature

make use of this strategy [60,61,63,94,101]. Therefore, the PGE doped graphene were modelled by substituting one carbon atom at the position M (Figure 3.1(b)) with Ru, Rh, Pd, Os, Ir and Pt and are represented by Gr-Ru, Gr-Rh, Gr-Pd, Gr-Os, Gr-Ir and Gr-Pt respectively whereas pristine graphene is denoted by p-Gr. The present work explores the effects of doping graphene with PGE with emphasis on the changes induced when PGE binds with neighbouring carbon atoms (carbon-PGE interaction), hence the edge effects are not taken into consideration. The PGE-doped graphene is thus composed of 23 carbon atoms, 12 hydrogen atoms and one PGE.

All the molecules were drawn using the visualisation tool GaussView 5 [103]. Multiwfn [104] program has been used for post processing and for obtaining data of density of states (DOS). The plots of UV-Vis absorption spectra were obtained using GaussSum 3.0 software package[105].The parameters incorporated in this study are formation energy and stability, HOMO-LUMO energy gap, Density of states (DOS), UV-Visible absorption spectra, and Mulliken Population analysis.

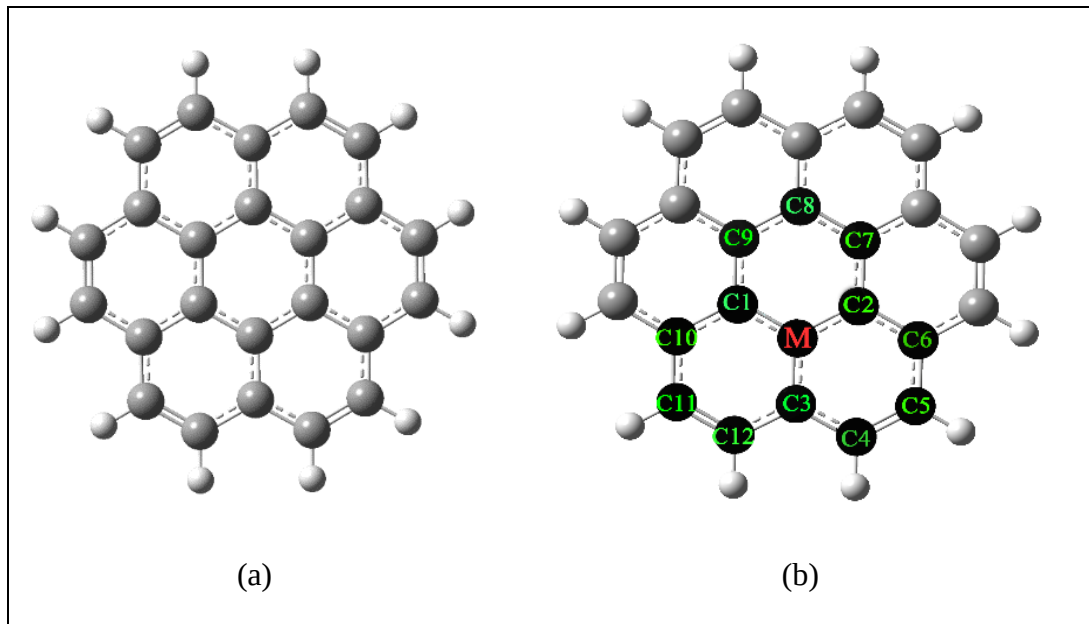


Figure 3.1. (a) Structure of graphene used in the study (b) PGE doped graphene (Here M= Carbon for pristine graphene and is doped with the PGE).

3.3 Results and discussions

3.3.1 Formation energy and structural stability

Formation energy is the energy required to break all bonds thereby dissociating the systems into its individual components. The more negative value of formation energy implies that a system is thermodynamically more stable whereas positive value indicates instability in the resultant system[106]. Before studying the structural, electronic and optical properties of pristine and PGE doped graphene, it is paramount to ascertain the structural stability of the molecules under study. In order to determine the stability of the structures, the formation energies of the structures has been calculated using Equation 3.1 [107,108] and the values are presented in Table 3.1.

$$E_{\text{form}} = E_{\text{system}} - xE_{\text{carbon}} - yE_{\text{hydrogen}} - zE_{\text{dopant}} \quad (3.1)$$

Where, E_{form} is the formation energy, E_{system} is the total energy of the optimised structure, E_{carbon} is the energy of carbon atom, E_{hydrogen} is the energy of hydrogen atom, E_{dopant} is the energy of the individual dopant (Ru, Rh, Pd, Os, Ir, Pt) and x, y, z are the number of carbon, hydrogen and dopant atoms in the structure. From Table 3.1, it can be inferred that incorporation of the dopants into graphene causes a slight decrease in the overall stability of the system. However, since the difference between the formation energies of pristine and doped graphene is considerably very low, it implies that the doped systems too would have almost the same stability like pristine graphene. The results of the calculation indicate that the p-Gr is the most stable and Gr-Pd is the least stable. The stability follows the order:

$$\text{p-Gr} > \text{Gr-Os} > \text{Gr-Ru} > \text{Gr-Ir} > \text{Gr-Rh} > \text{Gr-Pt} > \text{Gr-Pd}$$

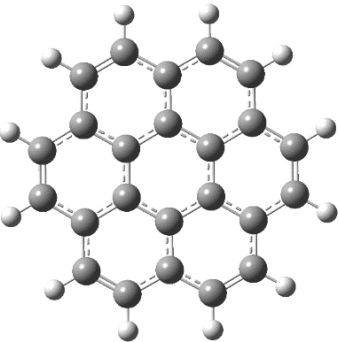
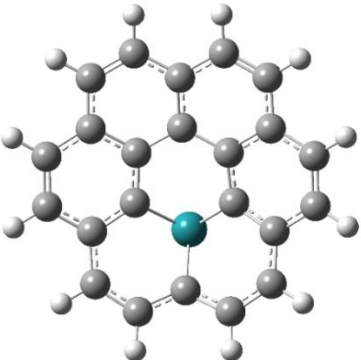
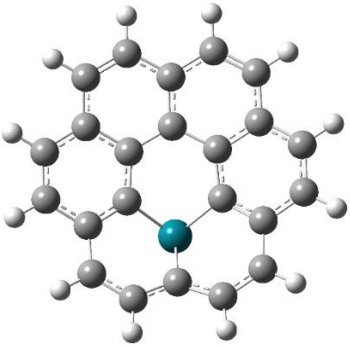
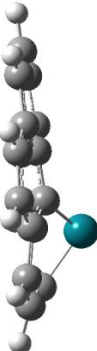
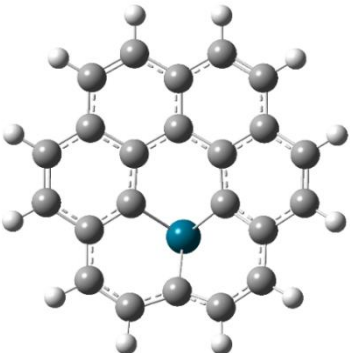
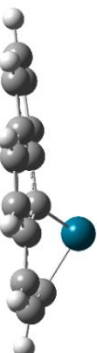
Table 3.1: The energy level of HOMO, LUMO molecular orbitals, E_{gap} and E_{form} calculated at B3PW91 level of theory and LANL2DZ basis set.

System	E_{H} (eV)	E_{L} (eV)	E_{gap} (eV)	E_{form} (eV)
p-Gr	-5.756	-1.686	4.070	-248.821
Gr-Ru	-5.061	-2.666	2.395	-241.817
Gr-Rh (alpha Molecular orbital)	-4.529	-1.629	2.900	-238.959

Gr-Pd	-4.538	-2.212	2.326	-235.945
Gr-Os	-4.926	-2.800	2.126	-242.922
Gr-Ir (alpha Molecular orbital)	-4.571	-1.697	2.874	-240.661
Gr-Pt	-4.547	-2.106	2.441	-238.552

3.3.2 Optimized structures and structural changes

Both front and side views of the optimised structures of pristine and doped graphene is shown in Figure 3.2. In all doped structures, graphene's surface is found to be distorted. It is observed that the PGE bulge out of the planar structure of graphene upon doping as can be seen in Figure 3.2. Further examination revealed that the bond length between the dopants and its surrounding carbon atoms is increased as compared to pristine graphene (p-Gr) (C-C bond length=1.43 Å). For Gr-Ru, the average Ru-C bond length (bond length between Ru, C1, C2, C3 as shown in Figure 3.1) is found to be 1.896 Å whereas for Gr-Rh, Gr-Pd, Gr-Os, Gr-Ir, Gr-Pt systems, the average M-C bond (where M=Rh, Pd, Os, Ir, Pt) length is 1.913 Å, 1.963 Å, 1.906 Å, 1.91 Å and 1.95 Å respectively. Furthermore, substitution of PGE into graphene resulted in significant variation in bond angles. For Gr-Ru, Gr-Rh, Gr-Pd, Gr-Os, Gr-Ir and Gr-Pt systems, the $\angle C-\angle M-\angle C$ (where M= Ru, Rh, Pd, Os, Ir, Pt) angle is around 93°, 93°, 92°, 94°, 95° and 94° respectively which is significantly less as compared to $\angle C-\angle C-\angle C$ bond angle of pristine graphene which is 120°. Due to the decrease in bond angle from 120° to 92-95°, the planar surface structure of graphene gets affected and the PGE (Pt, Rh, Ru, Ir, Os, Pd) bulge out of the surface of graphene. The detailed changes in bond lengths and bond angles for all the systems are listed in Table 3.2(a) and 3.2(b) respectively. The changes in bond lengths and bond angles may be attributed to the fact that the dopants influences the local bonding environment as a result of their electronegativity difference (2.55, 2.20, 2.28, 2.20, 2.20, 2.20, 2.28, for C, Ru, Rh, Pd, Os, Ir and Pt respectively)[109] and difference in the covalent radii (0.73 Å, 1.46 Å, 1.42 Å, 1.39 Å, 1.44 Å, 1.41 Å and 1.36 Å for C (sp²), Ru, Rh, Pd, Os, Ir and Pt respectively) [110].

Systems	Front view	Side view
p-Gr		
Gr-Ru		
Gr-Rh		
Gr-Pd		

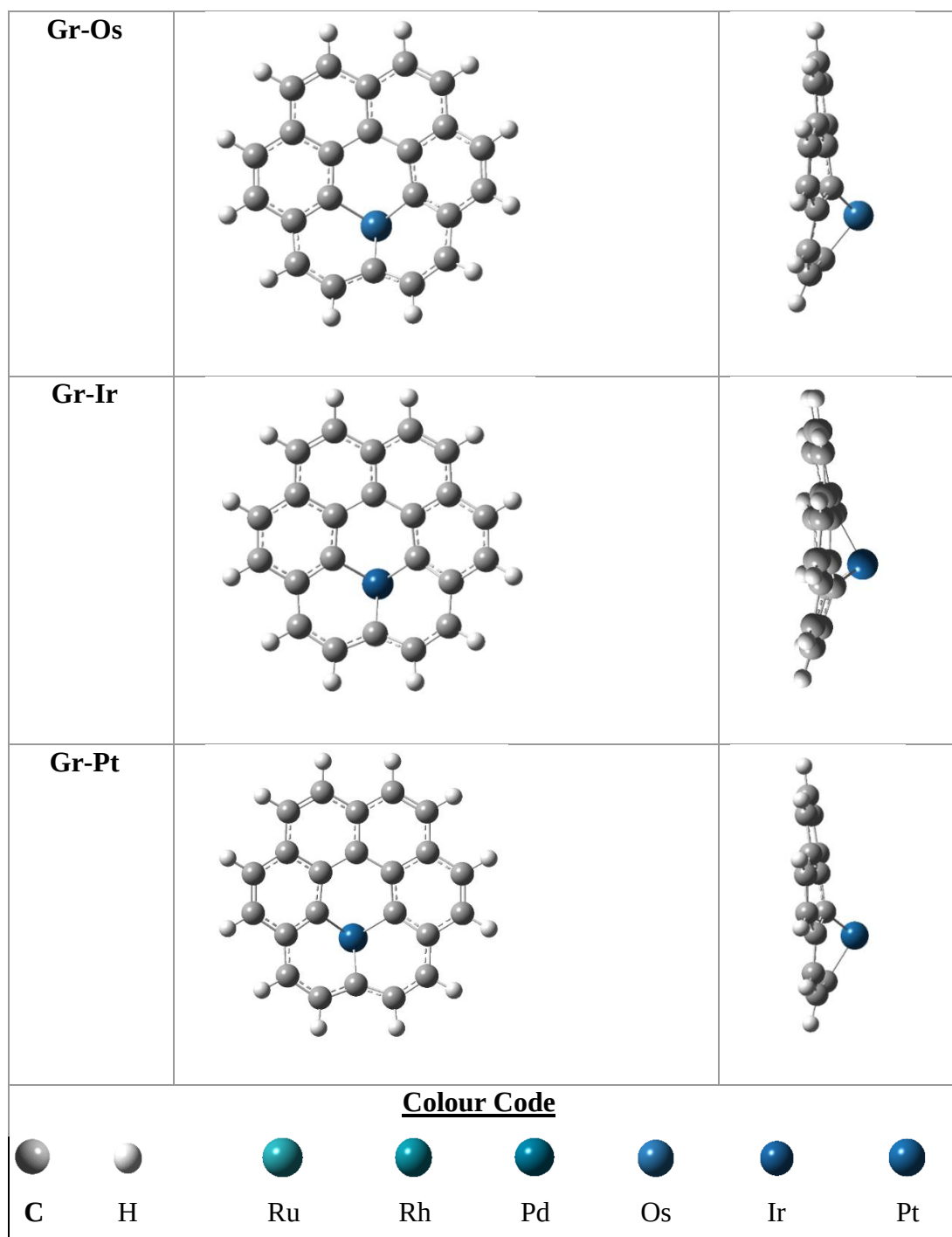


Figure 3.2. The optimised structures of all the systems optimised using B3PW91 level of theory and LANL2DZ basis set.

Table 3.2 (a): The bond lengths in Å, (M=C, Ru, Rh, Pd, Os, Ir and Pt in p-Gr, Gr-Ru, Gr-Rh, Gr-Pd, Gr-Os, Gr-Ir, Gr-Pt respectively) (C1, C2, C3, C4, C5, C6, C7, C8, C9, C10, C11, C12 are shown in Figure 3.1).

	pGr	Gr- Ru	Gr- Rh	Gr- Pd	Gr- Os	Gr- Ir	Gr- Pt
M- C1	1.43	1.90	1.91	1.96	1.91	1.91	1.95
M- C2	1.43	1.90	1.91	1.96	1.91	1.91	1.95
M-C3	1.42	1.89	1.92	1.97	1.90	1.91	1.95
C3-C4	1.43	1.43	1.42	1.41	1.44	1.43	1.42
C4-C5	1.38	1.39	1.39	1.38	1.39	1.39	1.39
C5-C6	1.43	1.44	1.45	1.44	1.44	1.45	1.44
C6-C2	1.42	1.42	1.41	1.40	1.43	1.42	1.41
C2-C7	1.43	1.43	1.42	1.41	1.44	1.42	1.41
C7-C8	1.43	1.45	1.45	1.44	1.45	1.45	1.44
C8-C9	1.43	1.45	1.45	1.44	1.45	1.45	1.44
C9-C1	1.43	1.43	1.42	1.41	1.44	1.42	1.41

C1-C10	1.42	1.42	1.41	1.40	1.43	1.42	1.41
C10-C11	1.43	1.44	1.45	1.44	1.44	1.45	1.44
C11-C12	1.38	1.39	1.39	1.38	1.39	1.39	1.39
C12-C3	1.43	1.43	1.42	1.41	1.44	1.43	1.42

Table. 3.2 (b): The bond angles of all systems (in degree) (M=C, Ru, Rh, Pd, Os, Ir and Pt in p-Gr, Gr-Ru, Gr-Rh, Gr-Pd, Gr-Os, Gr-Ir, Gr-Pt respectively).

	pGr	Gr- Ru	Gr- Rh	Gr- Pd	Gr- Os	Gr- Ir	Gr- Pt
C1-M-C2	119.99	92.14	91.27	85.83	93.36	92.59	89.42
C2-M-C3	120.00	93.83	93.71	92.02	94.58	95.10	94.48
C3-M-C1	119.99	93.83	93.71	92.02	94.58	95.11	94.48
M-C3-C4	119.99	117.45	115.58	114.10	117.64	115.99	114.14
M-C3-C12	118.94	117.45	115.58	114.10	117.64	115.99	114.14
C3-C4-C5	121.05	123.05	124.22	127.01	123.26	124.14	126.49
C4-C5-C6	121.06	126.23	125.14	123.40	126.77	126.15	124.85

C5-C6-C2	118.93	120.20	121.29	123.16	120.30	121.21	122.77
M-C2-C6	119.99	119.24	117.72	115.95	119.58	118.17	116.60
M-C2-C7	120.00	119.47	118.63	116.20	119.44	118.87	117.41
C2-C7-C8	120.00	122.18	122.69	123.08	122.42	122.70	123.32
C7-C8-C9	119.99	122.71	122.06	120.40	123.29	122.79	121.67
C8-C9-C1	120.00	122.18	122.69	123.08	122.42	122.70	123.32
M-C1-C9	120.00	119.47	118.63	116.20	119.44	118.87	117.41
M-C1-C10	119.99	119.24	117.72	115.95	119.58	118.17	116.60
C1-C10-C11	118.94	120.20	121.29	123.16	120.30	121.21	122.77
C10-C11-C12	121.05	126.23	125.14	123.40	126.77	126.15	124.85
C11-C12-C3	121.05	123.05	124.22	127.01	123.26	124.14	126.49

3.3.3 HOMO-LUMO orbital analysis

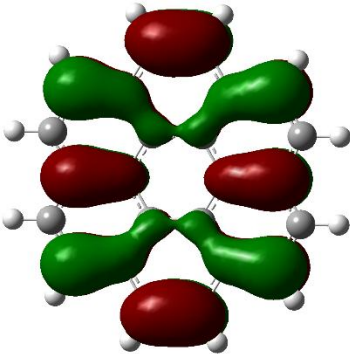
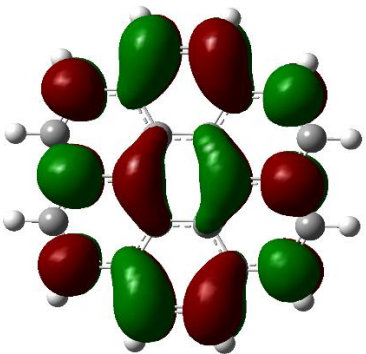
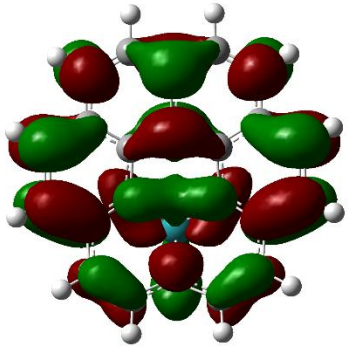
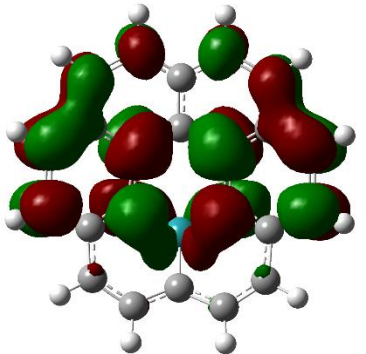
For the development of new materials for any optoelectronic applications, it is crucial to comprehend the fundamental electronic properties which is governed by the energy levels of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the energy gap (E_{gap}). Energy gap is the energy required to excite the electrons from the ground state to the first allowed excited state. To a good approximation, it can be described as the difference in energy between HOMO and LUMO orbitals and is calculated according to Equation 3.2.

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (3.2)$$

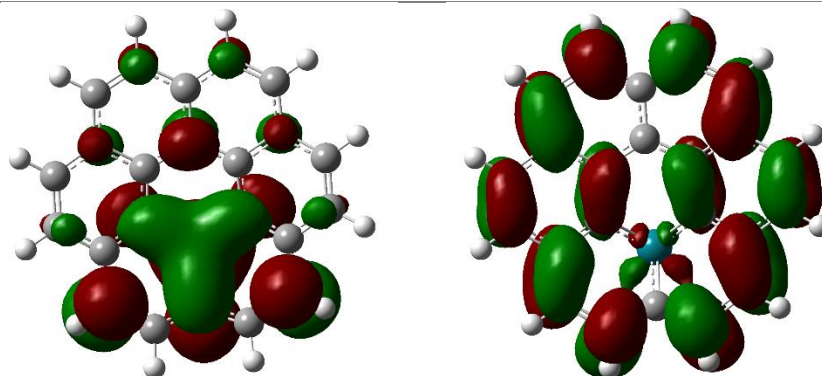
where, E_{gap} is the energy gap, E_{LUMO} and E_{HOMO} is the energy of the HOMO and LUMO molecular orbitals respectively. Modulating the energies of HOMO and LUMO is a significant challenge to design materials for use in optoelectronics. One way to alter the energies of HOMO and LUMO levels of carbon/graphene is by doping or substitution with heteroatoms; thus, it is paramount to understand the changes in these energy levels caused by substitution. For the development of any luminescent material, it is important to know the delocalization of molecular orbitals in order to ascertain which part of the system is capable of absorbing a photon and which part of the system undergoes electron density migration. Usually the portion where HOMO is located is capable of absorbing a photon and the electron density migrates to the LUMO portion [111] upon photon absorption. Furthermore, charge transport through a system is dependent on the extent of delocalization of molecular orbitals, energy gap and geometry of the system [112–114].

The localization of HOMO and LUMO orbitals of pristine and doped graphene are shown in Figure 3.3. Review of the LUMO orbitals (Figure 3.3) reveals that for p-Gr and Gr-Ru, the LUMO orbitals are localized on the entire surface whereas for Gr-Rh, Gr-Pd, Gr-Ir, Gr-Pt, it is densely localized near the dopants and for Gr-Os, the orbitals are more diffused and drawn towards Os. Inspection of the HOMO orbital diagrams reveals that for Gr-Pd and Gr-Pt, the orbitals are highly localized in the vicinity of the dopant whereas, it is spread out throughout the surface for p-Gr. For Gr-Rh and Gr-Ir, the orbitals are distributed all over the surface except near the dopant whereas for Gr-Ru and Gr-Os, the orbitals are more diffused near the dopant.

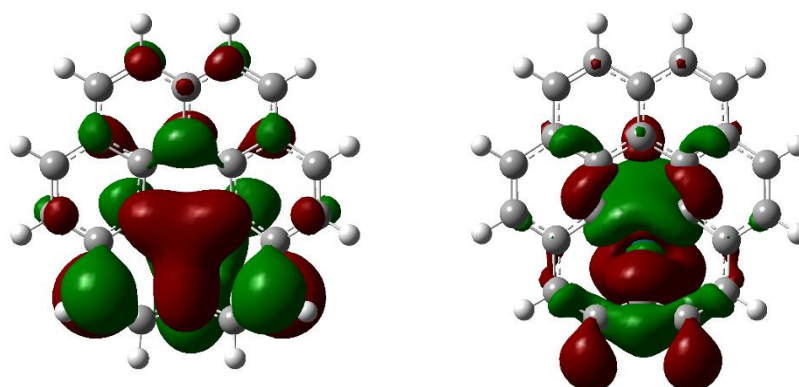
The calculated energy gap of the pristine and doped graphene is shown in Table 3.1. Usually, wider energy gap indicates reduced charge transfer and narrow (low) energy gap corresponds to enhanced charge transfer. From the energy gap calculation, it is observed that the inclusion of the PGE causes a decrease in the value of the energy gap which results in minimizing the barrier for electron transport in the system leading to an increase in the number of π mobile electrons indicating enhanced conductivity and charge transport [112]. The energy gap is found to be the highest for p-Gr and lowest for Gr-Os. Therefore, it can be inferred that these dopants could well be incorporated for the fabrication of materials where a small band gap, increased conductivity and high mobility of π electrons are desired.

Systems	HOMO	LUMO
p-Gr		
Gr-Ru		

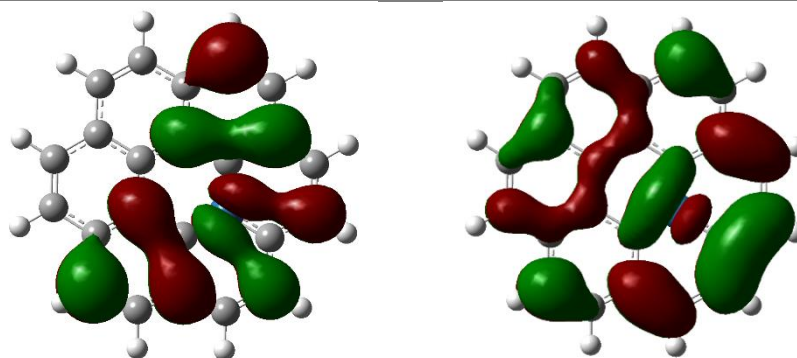
Gr-Rh



Gr-Pd



Gr-Os



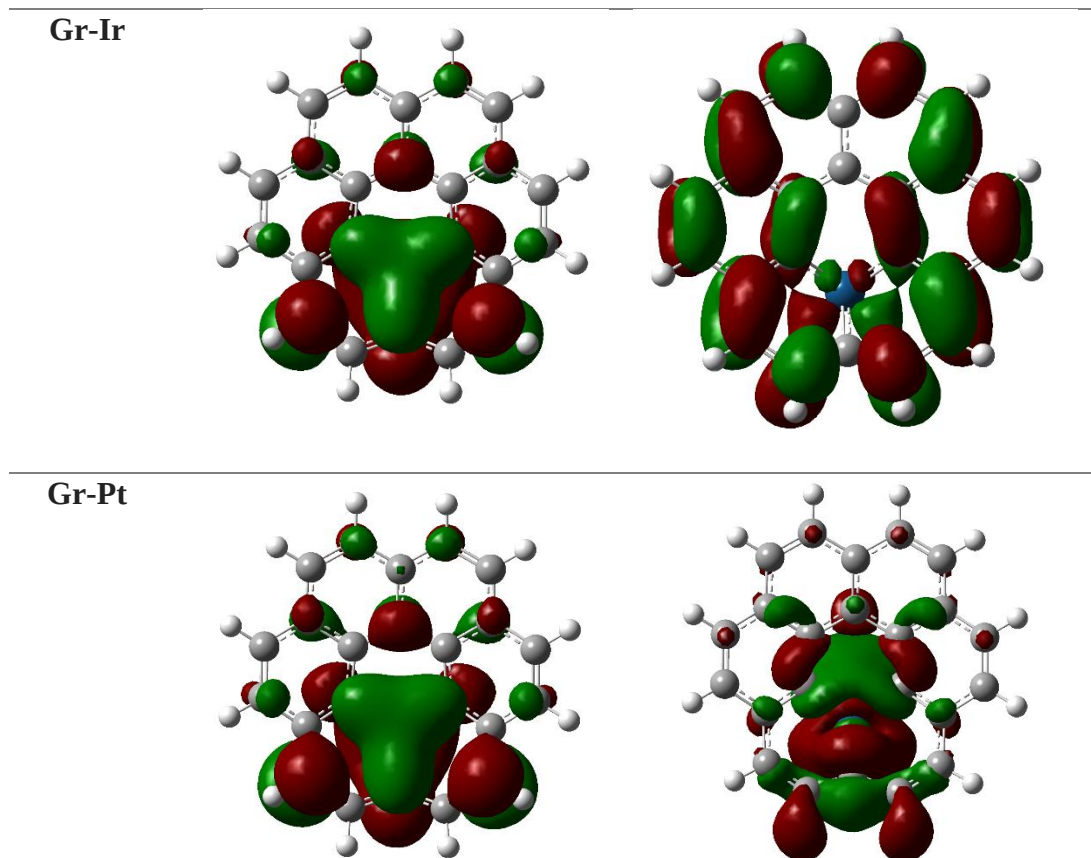
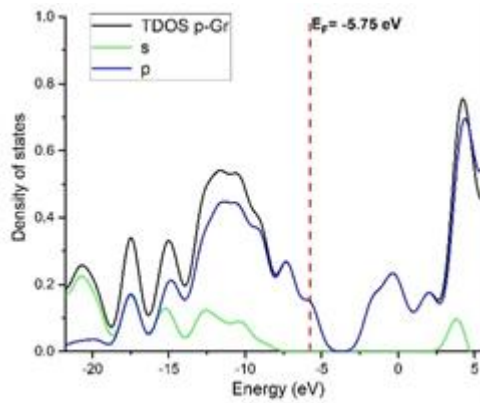


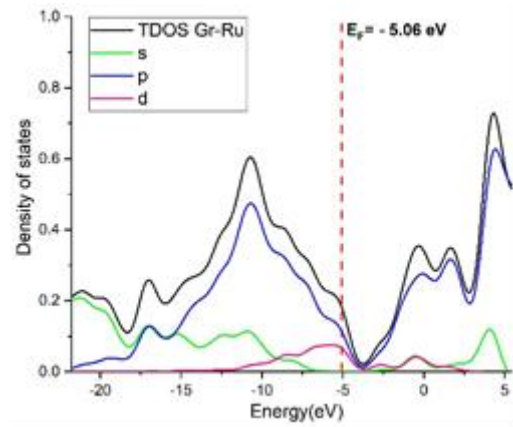
Figure 3.3. The localized HOMO and LUMO molecular orbitals of all the systems calculated at B3PW91 level of theory and LANL2DZ basis set.

3.3.4 Density of states (DOS)

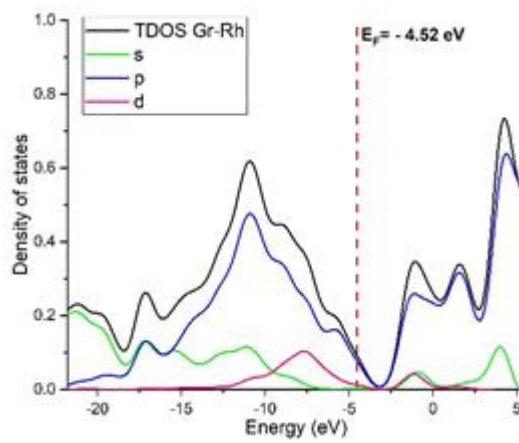
The density of states describes the number of different states of a system at a particular energy level that the electrons are allowed to occupy. The properties of materials such as paramagnetic susceptibility, specific heat, electrical conductivity etc. depends on DOS [115,116]. The electrons in graphene possesses unusual mobility which influences its role in various applications. DOS describes the concentrations and distribution of energy of the carriers. Therefore, inspection of the DOS gap at the Fermi level allows one to comment over the conducting property of a material [117]. Moreover, manipulation of the DOS enables one to boost device performance [118,119]. Thus, it is essential to comprehend DOS, Fermi level and the changes induced on them on doping to improve the performance of materials.



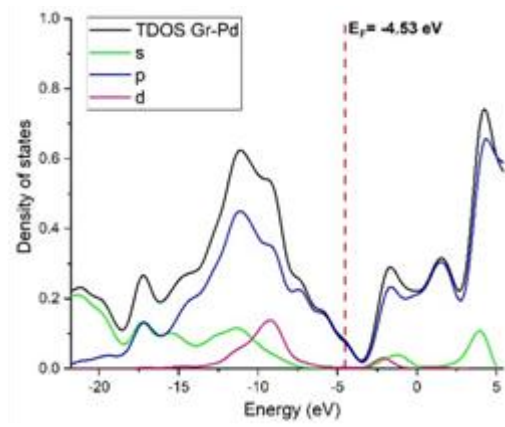
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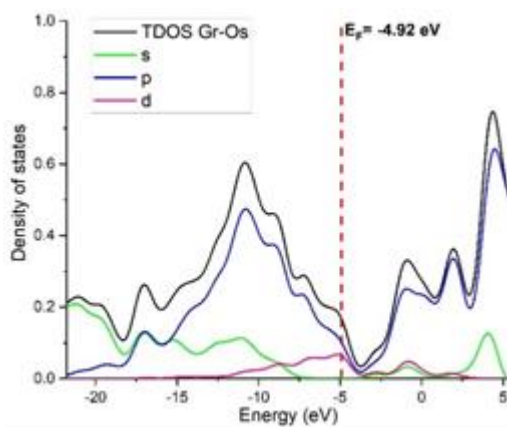
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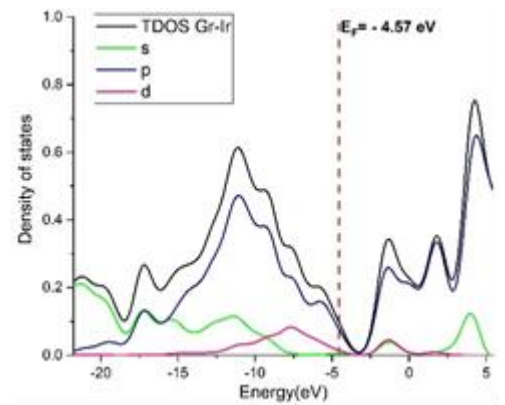
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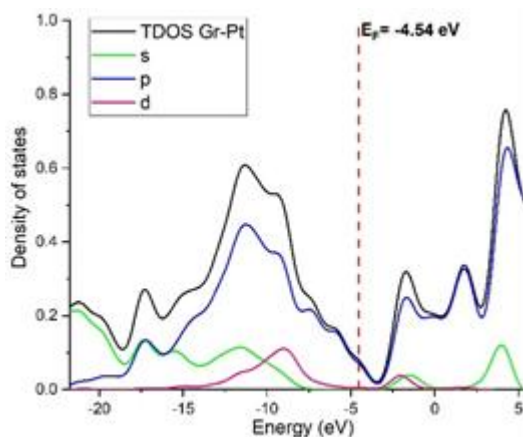
(d)



(e)



(f)



(g)

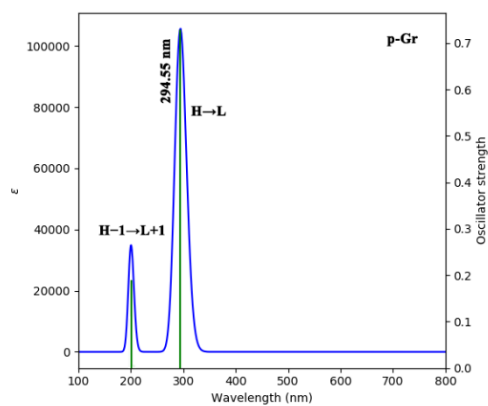
Figure 3.4. The total density of states (TDOS) along with projected density of states (PDOS) for (a) p-Gr (b) Gr-Ru (c) Gr-Rh (d) Gr-Pd (e) Gr-Os (f) Gr-Ir (g) Gr-Pt at B3PW91 level of theory and LANL2DZ basis set. The Fermi level is denoted by red dotted lines.

The total density of states (TDOS) (black curves in Figure 3.4) and the projected density of states (PDOS) of pristine and doped graphene are shown in Figure 3.4. For p-Gr, it is found that the Fermi energy (E_F , shown by red dotted line) coincides with E_{HOMO} at -5.75 eV (Figure 3.4(a)). Doping graphene with the PGE significantly shifts the Fermi level. It is observed that the Fermi level decreases for all the doped systems by varying degrees. The Fermi level shifts to -5.06 for Gr-Ru, -4.52 for Gr-Rh, -4.53 eV for Gr-Pd, -4.92 for Gr-Os, -4.57 for Gr-Ir and -4.54 eV for Gr-Pt respectively. The contribution of different orbitals towards the total DOS can be studied by PDOS graph which is shown alongside TDOS in Figure 3.4. Analysis of the PDOS graph for p-Gr indicates that near the Fermi level, the main contribution comes from the p-orbital electrons because of the formation of sp^2 hybridised π electron cloud. Figure 3.4 (b)-(f) indicates that even after doping, the main contribution is from the p-orbital (blue curves in Figure 3.4) electrons however the s-orbital (green curves in Figure 3.4) and the d-orbital (purple curves in Figure 3.4) electron also contributes to some extent towards TDOS near the fermi level. Analysis of Figure 3.4 reveals that for Gr-Os (Figure 3.4(c)) and Gr-Ru (Figure 3.4(g)) the contribution of the d-orbital electrons (shown by purple curves) is significantly more

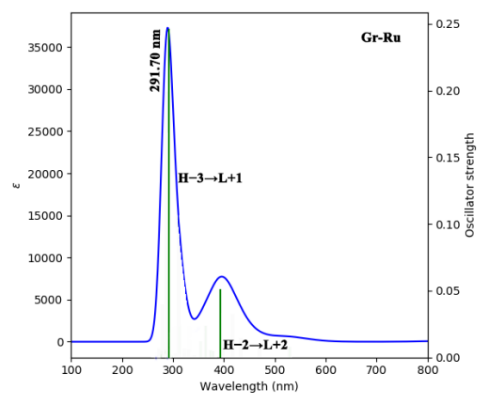
near the Fermi level and is almost comparable to the p-orbital electron's contribution, while the d-orbital density is comparatively less in the cases of Gr-Ir and Gr-Rh. For Gr-Pd and Gr-Pt, the contribution of d-orbital electrons is almost zero near the Fermi level. Therefore, from the results it can be inferred that incorporation of Ru and Os into the hexagonal carbon lattice can effectively increase the density of states near the Fermi level.

3.3.5 UV–Vis absorption spectra

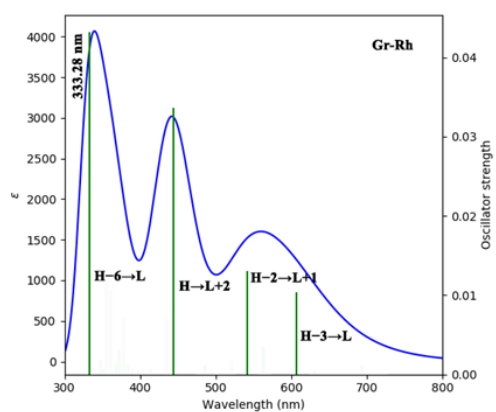
The absorption characteristic of a material determines its efficacy and suitability for the development of any optoelectronic device; therefore, it was thought important to study the absorption spectra of the PGE doped graphene. TD-DFT was employed to obtain the UV-visible absorption spectrum of all the systems in gas phase [120–126]. In order to ascertain the shifting of the absorption wavelength, pristine graphene is taken as a reference. The UV-visible spectra of all the systems are shown in Figure 3.5 and the resultant parameters obtained by TD-DFT calculations are shown in Table 3.3. Analysis of Table 3.3 reveals that maximum absorption ($\lambda_{\max}$) obtained for pristine graphene is at 294.55 nm (oscillator strength (f) = 0.73). It is observed that the position and intensity of $\lambda_{\max}$ changes significantly upon doping with PGE. The value of $\lambda_{\max}$ is shifted to 291.70 nm ($f=0.25$), 333.28 nm ($f=0.04$), 306.27 nm ($f=0.25$), 299.37 nm ($f=0.13$), 478.76 nm ($f=0.03$), and 308.29 nm ($f=0.26$) for Gr-Ru, Gr-Rh, Gr-Pd, Gr-Os, Gr-Ir, Gr-Pt systems respectively. Thus, it can also be deduced that the values of the shifting of $\lambda_{\max}$ increases in the order: Gr-Ru > p-Gr > Gr-Os > Gr-Pd > Gr-Pt > Gr-Rh > Gr-Ir. Furthermore, the subsequent high-energy transitions at 200.88 nm ($f=0.19$), 393.83 nm ($f=0.01$), 443.74 nm ($f=0.03$), 445.65 nm ($f=0.05$), 418.01 nm ($f=0.06$), 350.39 nm ($f=0.03$), 470.5 nm ($f=0.07$) is responsible for the other peak for p-Gr, Gr-Ru, Gr-Rh, Gr-Pd, Gr-Os, Gr-Ir, Gr-Pt systems respectively. Therefore, it can be inferred that introduction of Ru in graphene results in hypsochromic shift (blue shift) whereas Rh, Pd, Os, Ir and Pt causes bathochromic shift (red shift). This variation in $\lambda_{\max}$ values implies doping with PGE could be used to tailor and control $\lambda_{\max}$ as per the requirement.



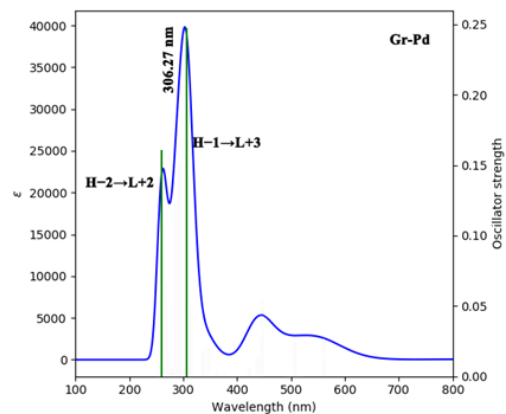
(a)



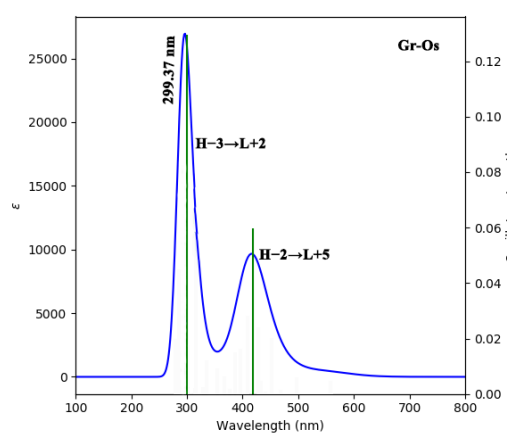
(b)



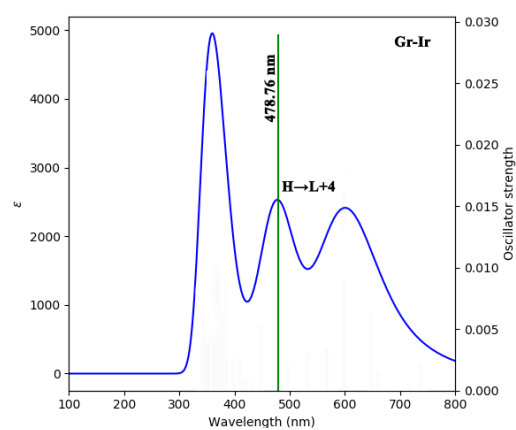
(c)



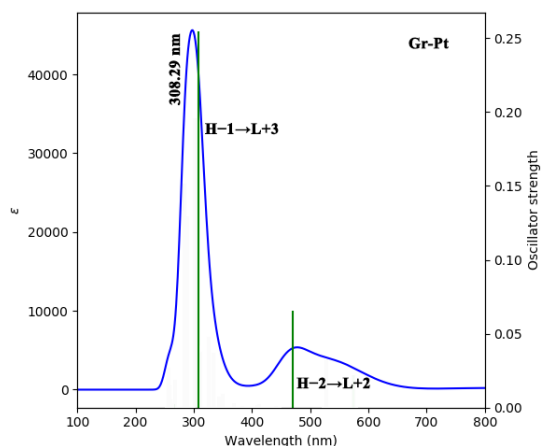
(d)



(e)



(f)



(g)

Figure 3.5. UV Vis absorption spectrum (a) p-Gr (b) Gr-Ru (c) Gr-Rh (d) Gr-Pd (e) Gr-Os (f) Gr-Ir (g) Gr-Pt calculated using TD DFT at B3PW91/LAN2DZ level of theory.

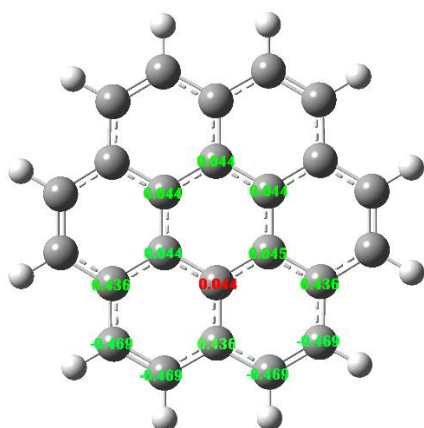
3.3.6 Mulliken Population Analysis

To understand the effect of doping on the charge-density distribution, Mulliken population analysis has been studied because the distribution of atomic charges affects the electronic properties of systems, dipole moment and other properties considerably. It has also been computed to get an insight into the transfer of the effective atomic charges from the dopants to adjacent carbon atoms. The distribution of charges on the dopants and on the atoms around the doped region are shown in Figure 3.6. Analysis of Figure 3.6 revealed that the charges on C atom (present at position M), Ru, Rh, Pd, Os, Ir, Pt are +0.044e, +0.332e, +0.321e, +0.229e, +0.752e, +0.649e, +0.555e for p-Gr, Gr-Ru, Gr-Rh, Gr-Pd, Gr-Os, Gr-Ir, and Gr-Pt respectively. The introduction of PGE causes significant changes in the charge distribution around C1, C2, and C3. The charges on C1, C2 and C3 are found to be +0.044e, +0.045e, +0.436e for p-Gr.

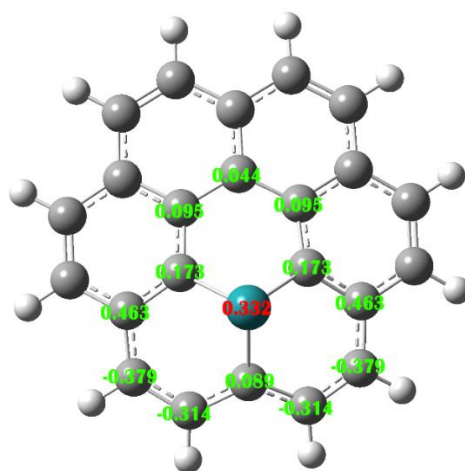
Table 3. 3: UV Vis parameters for doped graphene by TD- DFT calculations.

Systems	Maximum absorption wavelength (λ_{max}) (nm)	Absorption Energy (eV)	Oscillator strength (f)	ΔE shifting in eV	Symmetry	Electronic Transition Contribution
p-Gr	294.55	4.20	0.730	-	Symmetry A	(77) H-1 $\rightarrow$ (80) L+1 (44%), (78) H $\rightarrow$ (79) L (44%)
Gr-Ru	291.70	4.25	0.246	-0.05	Symmetry A	(80) H-3 $\rightarrow$ (85) L+1 (28%), (81) H-2 $\rightarrow$ (86) L+2 (19%)
Gr-Rh	333.28	3.72	0.043	0.48	-	(82) H-2 $\rightarrow$ (86) L+1 (14%), (81) H-3 $\rightarrow$ (85) L (8%) (α - α amplitudes); (77) H-6 $\rightarrow$ (84) L (29%), (83) H $\rightarrow$ (86) L+2 (15%) (β - β amplitudes)
Gr-Pd	306.27	4.05	0.248	0.15	Symmetry A	(83) H-1 $\rightarrow$ (88) L+3 (29%), (82) H-2 $\rightarrow$ (87) L+2 (26%)
Gr-Os	299.37	4.14	0.130	0.06	Symmetry A	(80) H-3 $\rightarrow$ (85) L+2 (30%), (81) H-2 $\rightarrow$ (89) L+5 (21%)
Gr-Ir	478.76	2.59	0.029	1.61	-	(84) H $\rightarrow$ (89) L+4 (85%)
Gr-Pt	308.29	4.11	0.255	0.09	Symmetry A	(83) H-1 $\rightarrow$ (88) L+3 (23%), (82) H-2 $\rightarrow$ (87) L+2 (21%), (83) H-1 $\rightarrow$ (89) L+4 (20%)

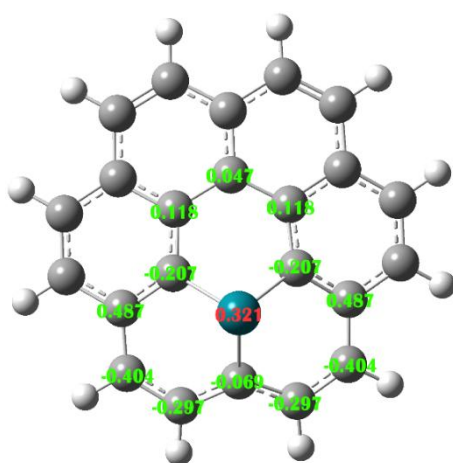
For Gr-Os, Gr-Ir and Gr-Pt, all three adjacent (C1, C2 and C3) atoms show negative charges with values of $-0.308e$, $-0.0308e$, $-0.020e$ for Gr-Os; $-0.348e$, $-0.348e$, $-0.040e$ for Gr-Ir; and $-0.376e$, $-0.376e$, $-0.042e$ for Gr-Pt respectively. The charges on C1 and C2 for Gr-Os, Gr-Ir, and Gr-Pt were observed to be identical. On the other hand, for Gr-Ru, Gr-Rh, and Gr-Pd systems, one of the carbon atoms (C3) exhibits a positive charge whereas C1 and C2 bore negative charges. The computed charges on C1, C2 and C3 are $-0.173e$, $-0.173e$, $+0.089e$ for Gr-Ru, $-0.207e$, $-0.207e$, $+0.069e$ for Gr-Rh, and $-0.214e$, $-0.214e$, $+0.029e$ for Gr-Pd respectively. Considering the charge distribution of p-Gr as a reference, it can be inferred from Table 3.4 and Figure 3.6 that introduction of Pt results in the largest distribution of charges ($-0.376e$, $-0.376e$, $-0.042e$) whereas introduction of Ru results in the lowest distribution of charges ($-0.173e$, $-0.173e$, $+0.089e$) on C1, C2, and C3 respectively. The variation in the charge distribution in case of the doped systems could be attributed to the differences in electronegativity of the (2.55, 2.20, 2.28, 2.20, 2.20, 2.20, 2.28, for C, Ru, Rh, Pd, Os, Ir and Pt respectively) [109]. In addition, the number of valence electrons (4, 8, 9, 10, 8, 9, 10, valence electrons for C, Ru, Rh, Pd, Os, Ir and Pt respectively) [127], and the presence of additional lone pairs for PGE as compared to the carbon atom in p-Gr [128] could also be a contributing factor. The presence of positive and negative regions could facilitate better charge transfer [129], compared to p-Gr which in turn has a profound effect on the energy gap, maximum absorption wavelength ($\lambda_{\max}$) and other properties of the systems [130]. Since, doping with PGE alters the charge-density distribution, therefore, it affects the electronic properties of the doped systems which is also evident from HOMO-LUMO orbital analysis, density of states (DOS) analysis and UV-Visible adsorption studies.



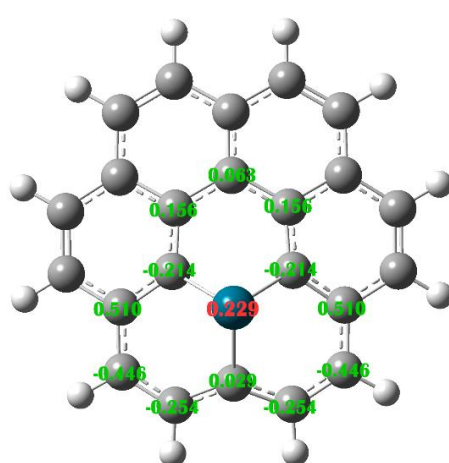
(a)



(b)



(c)



(d)

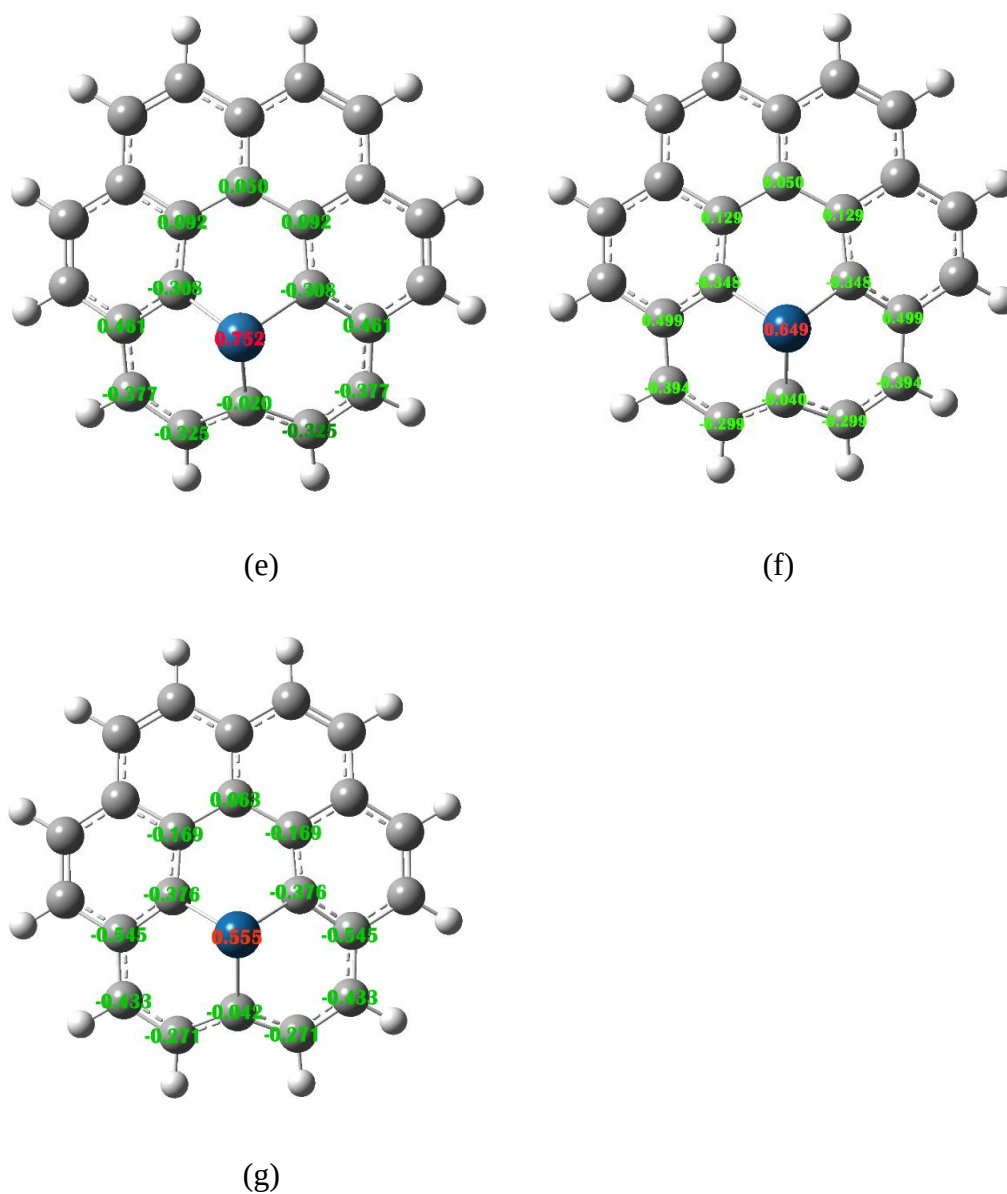


Figure 3.6. The atomic distribution of charges on the atoms around the doped region for (a) p-Gr, (b) Gr-Ru, (c) Gr-Rh, (d) Gr-Pd, (e) Gr-Os, (f) Gr-Ir, and (g) Gr-Pt calculated at B3PW91/LANL2DZ level of theory (Only the significant charge alterations have been shown).

 Table 3.4: The charge distribution of PGE and neighbouring carbon atoms calculated at B3PW91/LANL2DZ level of theory.

Species	M= C	M=Ru	M= Rh	M=Pd	M=Os	M= Ir	M= Pt
M	0.044	0.332	0.321	0.229	0.752	0.649	0.555
C1	+0.044	-0.173	-0.207	-0.214	-0.308	-0.348	-0.376
C2	+0.045	-0.173	-0.207	-0.214	-0.308	-0.348	-0.376
C3	+0.436	+0.089	+0.069	+0.029	-0.020	-0.040	-0.042

3.4 Conclusion

In the present study, we used the density functional theory with B3PW91/ LANL2DZ method to theoretically analyse the structural, optical and electronic properties of pristine graphene and the effect on these properties when doped with Ru, Rh, Pd, Os, Ir and Pt. The study was carried out to comprehend and assist the development of novel materials with desired electronic and optical properties. The concluding comments are:

- Results of the formation energy calculation revealed that doping PGE causes an insignificant decrease in the overall stability of the molecules following the order p-Gr>Gr-Os>Gr-Ru>Gr-Ir>Gr-Rh>Gr-Pt>Gr-Pd.
- The incorporation of these dopants resulted in significant changes in the bond lengths (1.89–1.96 Å in doped systems as compared to 1.42–1.43 Å in p-Gr) and bond angles (85.83°–95.11° compared to 120° in p-Gr) thereby leading to structural deformities in graphene.
- The HOMO-LUMO orbital analysis revealed that the energy gap decreases for all the doped systems. The calculated energy gap of the doped systems is in the range 2.126 – 2.900 eV whereas in the case of p-Gr, it was found to be 4.070 eV.
- Mulliken population analysis showed that doping with PGE results in variation in charge distribution over the graphene. The charges on the neighboring carbon atoms of the dopants were found to vary from +0.089e to –0.376e.
- The density of states analysis showed that the Fermi level decreases for all the doped systems. PDOS analysis revealed that the density of states near the Fermi level significantly increases after Ru and Os doping.
- The UV-Visible absorption spectra were studied using the TD-DFT method. The results indicate substantial changes in the spectra as well as changes in maximum adsorption wavelength (λ_{max}). The maximum absorption wavelength was found to be in the range 291.70 nm to 478.76 nm for the doped systems whereas it was 294.55 nm for pristine graphene.

From the results, it was observed that doping of p-Gr with the PGE lead to various changes in the properties of the graphene. Due to their tailorable properties, the platinum

group doped graphene can be utilized for designing novel materials for different applications like wearable electronics, optoelectronics, sensors, energy storage devices, solar cells, etc. In conclusion, it is expected that the doping of graphene with platinum group elements might open new avenues for fine-tuning and enhancing the electronic and optical properties of graphene.

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Chapter 4

Scalable one-pot synthesis
of aminated reduced
graphene oxide for high-
performance supercapacitor
electrodes

CHAPTER 4

Scalable one-pot synthesis of aminated reduced graphene oxide for high-performance supercapacitor electrodes

4.1 Introduction⁺

The increasing reliance on non-renewable energy sources, from individual households to large-scale industries, highlights the pressing need for advanced energy storage solutions. These devices enable efficient storage of energy from renewable sources, such as sunlight and wind, ensuring its availability for future use. Despite variations in their methods of storing and delivering energy, most energy storage devices share a common purpose: to store charge [1]. Among these, supercapacitors stand out for their ability to rapidly store and discharge energy [2]. Supercapacitors store energy through two main mechanisms: electrical double-layer (EDL) capacitance and pseudocapacitance. EDL capacitors utilize electrode materials with a high surface area, where energy is stored through the accumulation of charges at the interface between the electrode and electrolyte. Since EDL-based supercapacitors do not involve physical changes in the electrodes during operation, they can sustain millions of charge and discharge cycles with minimal degradation in performance [2]. Pseudocapacitors, on the other hand, store energy via reversible Faradaic redox reactions. Materials with pseudocapacitive properties, such as MXenes, polyaniline, offer significantly higher energy densities compared to EDL-based supercapacitors. However, the Faradaic reactions occurring in pseudocapacitive electrodes can cause phase changes, which may reduce their lifespan and power density [3,4]. Additionally, EDL capacitors have faster response times compared to pseudocapacitors, making them better suited for applications that require rapid energy storage and release [4].

A highly promising electrode material for EDL capacitors is graphene, a 2D allotrope of carbon with sp^2 -hybridized carbon atoms arranged in a hexagonal lattice [5]. Its exceptional optical, mechanical, and electrical properties have generated significant interest, fueling the advancement of numerous applications [2,6].

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These include drug delivery [7], biochemical and electrochemical sensors [8], optoelectronic and microelectronic devices [9], and energy storage devices [10]. Although graphene possesses remarkable properties, its widespread use has been hindered by difficulties in large-scale production and its limited reactivity due to the lack of functional groups on its surface [11,12]. However, recent progress in the mass production of graphene and its derivatives, including graphene oxide (GO), reduced graphene oxide (rGO), and functionalized graphene nanosheets, has helped to overcome many of these challenges [13–15]. Chemically modified and functionalized graphene has become a key focus of research in graphene-based materials, particularly for applications in supercapacitors [16–21]. The growing interest in graphene functionalization stems from the potential to tailor its physical and chemical properties by adding specific organic groups to either the basal plane or the edges of graphene. Studies suggest that incorporating chemically reactive species, like amines [22,23], modifies the reactivity and chemistry of graphene's surface, thereby tremendously increasing the performance of graphene-based catalysts, energy storage devices, gas sensors, and biosensors [24–26]. Additionally, functionalization aids in the effective dispersion of graphene in common solvents, tackling a major difficulty in processing graphene-based materials [27]. As a result, significant efforts are being made to covalently modify graphene with various functional groups, thereby considerably expanding the family of functionalized graphenes.

Nitrogen is a common heteroatom that can be introduced into graphene through thermal treatment to enhance its performance in supercapacitors [28–30]. However, the high-temperature treatment, typically results in the formation of nitrogen functionalities, such as pyrrolic, pyridinic, quaternary, or pyridinic-N-oxides [12,31,32]. While these nitrogen substitutions enhance performance, they can also lead to poor wettability and chemical reactivity, which require further chemical modifications. Unlike nitrogen substitution, primary amines can be introduced into graphene sheets as ionizable functional groups, which could further improve the supercapacitor's electrochemical properties [12]. These ionizable groups have the potential to enhance the uniform and stable dispersion of graphene, facilitating its assembly or interaction with various polymers, organic molecules, and biological

systems, including DNA as well as fullerenes or carboxylated carbon nanotubes [11,12,33]. Furthermore, due to the electron-withdrawing tendency of amines, functionalizing graphene with amines alters the electronic structure, enhancing conductivity and allowing for precise engineering of work function [34]. As a result, aminated graphene is considered a suitable material for numerous fields ranging from drug delivery, photovoltaics, sensing and energy storage [12,35–37].

Several approaches have been developed to prepare aminated reduced graphene oxide ($\text{NH}_2\text{-rGO}$). For instance, Lai et al. [12] demonstrated successful functionalization with a primary amine through a single-step solvothermal process, utilizing ethane-1,2-diol as the solvent and ammonia as the nitrogen source. However, the process takes > 200 hours, involves multiple steps, and operates at a high temperature of 180°C for 10 hours. Furthermore, an analysis of the XRD data reveals that the characteristic features of GO are retained, indicating incomplete reduction. Similarly, Zhang and colleagues [37] produced amino-functionalized graphene oxide through Hoffman rearrangement, starting with GO and achieving an amine concentration of ~ 4%. The reaction takes ~ 47 hours and involves multiple steps, making it unsuitable for large-scale production. In another report, Rabchinskii et al. [32] synthesized aminated reduced graphene oxide following a two-step process. GO was initially brominated with hydrobromic acid followed by subsequent treatment with ammonia, yielding ~ 4% amination degree. However, this method makes use of toxic chemicals, entails the use of high temperatures, is time-consuming (~70 hours), has multiple steps and requires additional processing. Furthermore, using high temperatures results in the inclusion of nitrogen-containing heterocycles such as pyrroles, quaternary or pyridinic-N-oxides and pyridines rather than the formation of amines [12]. Therefore, there is a growing demand for environmentally friendly methods that enable high-yield synthesis of $\text{NH}_2\text{-rGO}$, at a reasonable cost for various applications. These methods not only need to be cost-effective but also sustainable, aligning with the current push toward greener technologies and practices in material production. As a result, researchers are focused on developing efficient, scalable, and eco-friendly approaches to meet these rising industrial demands.

In light of the above, we report, for the first time, a simple, one-pot, eco-friendly, and scalable method for preparing $\text{NH}_2\text{-rGO}$ in a record time of approximately 9 hours, making it the fastest method reported to date. This approach avoids the use of high temperatures, pressures, and toxic chemicals. It also achieves a high degree of amination ($\sim 6\%$), with the nitrogen content controllable by adjusting the pH of the reaction mixture (RM). The success of this method has been confirmed through X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), and energy dispersive X-ray (EDX) spectroscopic studies. The surface morphology of the $\text{NH}_2\text{-rGO}$ was analyzed using scanning electron microscopy (SEM). Furthermore, the incorporation of amine groups enhances the wettability of rGO, making it an excellent electrochemical material. The effect of this functionalization has been systematically studied to evaluate the potential $\text{NH}_2\text{-rGO}$ as supercapacitor electrodes. Variants of $\text{NH}_2\text{-rGO}$ —namely A-5, A-7, A-9, and A-12 (see Synthesis of $\text{NH}_2\text{-rGO}$ Section for the adopted nomenclature in this work)—show significant improvements compared to unfunctionalized rGO.

The symmetric supercapacitor fabricated with our as-synthesized material demonstrated (1) a significantly higher specific capacitance compared to rGO and similar materials, (2) exceptional charge-discharge cycling stability, with around 98% capacitance retention after 10,000 cycles of continuous operation, and (3) remarkable improvements in both gravimetric and volumetric energy and power densities, surpassing those of rGO by several-folds and even outperforming some binary composites. Additionally, the use of the ionic liquid 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF_4) in acetonitrile allowed us to overcome the limited electrochemical window of water-based electrolytes, expanding the operating voltage window to 2.2 V and thereby enhancing the potential for practical applications.

4.2 Materials and methods

4.2.1 Key resources

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals		
Graphite Powder	Sigma Aldrich	7782-42-5
Sulfuric acid ($\sim 98\%$)	Sigma Aldrich	7664-93-9

Potassium permanganate	Sigma Aldrich	7722-64-7
Ethanol	Sigma Aldrich	64-17-5
Ammonia solution extrapure AR, 30%	Sisco Research Laboratories Pvt. Ltd., India	1336-21-6
De-ionized water	Milli-Q	Resistivity 18.2 MΩ·cm @ 25 °C
L-Ascorbic acid AR, 99.7%	Sisco Research Laboratories Pvt. Ltd., India	50-81-7
Sodium Hydroxide Pellets ACS, 97%	Sisco Research Laboratories Pvt. Ltd., India	1310-73-2
1-Ethyl-3-Methylimidazolium Tetrafluoroborate (EMIM BF ₄) extrapure, 97%	Sisco Research Laboratories Pvt. Ltd., India	143314-16-3
Acetonitrile (ACN) ACS, 99.5%	Sisco Research Laboratories Pvt. Ltd., India	75-05-8
Poly(vinylidene fluoride) (average M _w ~534,000 by GPC, powder)	Sigma Aldrich	24937-79-9
N-Methyl-2-Pyrrolidone (NMP) extrapure AR, 99.5%	Sisco Research Laboratories Pvt. Ltd., India	872-50-4
Software and algorithms		
ImageJ	https://imagej.net/ij/index.html	https://www.nature.com/articles/nmeth.2089
OriginLab	https://www.originlab.com/	OriginPro 2024b (Learning Edition)
Other		
Autolab PGSTAT204 Electrochemical workstation	Metrohm	https://www.metrohm.com/en_in/products/aut20/aut204_s.html

4.2.2 Synthesis of NH₂-rGO

NH₂-rGO was synthesized using modified Hummer's method with some significant modifications [38]. In brief, 23 mL of concentrated H₂SO₄ was added to 1 g of graphite powder, and the RM was placed in an ice bath to maintain a low temperature. NaNO₃ was not used in this synthesis because it emits toxic gases, which may be detrimental to large-scale production. Later, 6g KMnO₄ was slowly introduced in small proportions to the RM, ensuring that the temperature remained <10 °C with continuous stirring. Next, the RM was stirred at 35 °C for 30 minutes, and then 70 mL of de-

ionized H₂O was added. The RM was further subjected to sonication for 30 minutes and was stirred for another 30 minutes. At this stage, ammonia solution was added to the RM to adjust the pH, a crucial step that allows precise control over the concentration of nitrogen species incorporated into graphene. The pH was carefully controlled and set to specific values of 5, 7, 9, and 12, producing four distinct samples named A-5, A-7, A-9, and A-12, respectively. Subsequently, 100 mL of 1M L-ascorbic acid was introduced to the RM, and the mixture was refluxed at 95 °C for 1 hour to facilitate the reduction process. The reaction product was thoroughly washed with deionized water until the pH of the solution reached ~7 to remove any residual impurities. The resulting blackish powder solid was dried at 50 °C to produce NH₂-rGO.

In order to make a comparison, we synthesized reduced graphene oxide using the same process except in this case, we used NaOH to adjust the pH to ~7 and was washed with 5% HCl and DI H₂O. The other experimental conditions are the same. The prepared materials were subsequently characterized using a range of analytical techniques.

4.2.3 Materials characterization

Powder X-ray diffraction was recorded using a Philips X'pert Pro X-ray diffractometer with Cu K α radiation ($k = 1.54056 \text{ \AA}$). Scanning electron microscope images were obtained with field-emission scanning electron microscope (JSM 7900F, JEOL). Infrared transmission spectra were recorded with a Perkin Elmer Spectrum Two Fourier-transform infrared spectrometer with ATR in the 450-4000 cm⁻¹ range with a resolution of 1 cm⁻¹. X-ray photoelectron spectroscopy measurements were made using Thermofisher Nexsa system employing an Al K α X-ray source (1486.6 eV).

4.2.4 Electrochemical studies

All electrochemical measurements were performed on an Autolab PGSTAT204 electrochemical workstation (Metrohm, The Netherlands) with 1 M EMIMBF₄ in acetonitrile as the electrolyte. Both three-electrode and two-electrode configurations were used to evaluate the electrochemical performance. In the three-electrode setup, a

platinum mesh (area =1 cm × 1 cm) served as the counter electrode, and a Ag/Ag⁺ non-aqueous electrode filled with a 2 M LiCl solution in ethanol was used as the reference electrode. The working electrodes were prepared by blending the active material, poly(vinylidene fluoride) (PVDF) and carbon black in a ratio of 85:10:5 in a mortar with NMP solvent, and then ground with a pestle. The resulting slurry was coated onto a graphite sheet (1 cm × 1 cm) and vacuum dried at 70 °C for 16 hours. The three-electrode measurements were conducted at room temperature (27 °C ± 3).

CV and GCD were carried out at different scan rates and current densities across a potential window of 0 to 2.2 V and −0.6 to 1.2 V for two-electrode and three-electrode systems, respectively. EIS measurements were conducted with an amplitude of 10 mV over a frequency range of 0.1 Hz to 10 kHz at OCP.

Equations 4.1 and 4.2 were utilized to determine C_S (F g^{−1}) from the CV and GCD data in the three-electrode configuration [39,40]. The capacitance of the graphite sheet was neglected.

$$C_S = \frac{A}{\Delta V \times v \times m} \quad (4.1)$$

$$C_S = \frac{I \times \Delta t}{m \times \Delta V} \quad (4.2)$$

Where, A, ΔV , v , m , Δt and $\frac{I}{m}$ represents the integral area of CV loops, sweep potential window (V), scan rate (V s^{−1}), mass of electrodes (g), discharging time (s) and applied current density (A g^{−1}), respectively.

Equations 4.3 and 4.4 were utilized to determine the C_S (F g^{−1}) from the CV and GCD data for the symmetric supercapacitor [41].

$$C_S = \frac{2A}{\Delta V \times v \times m} \quad (4.3)$$

$$C_S = \frac{2(I \times \Delta t)}{m \times V} \quad (4.4)$$

A factor of 2 is introduced to account for the series capacitance that arises in a symmetric supercapacitor device.

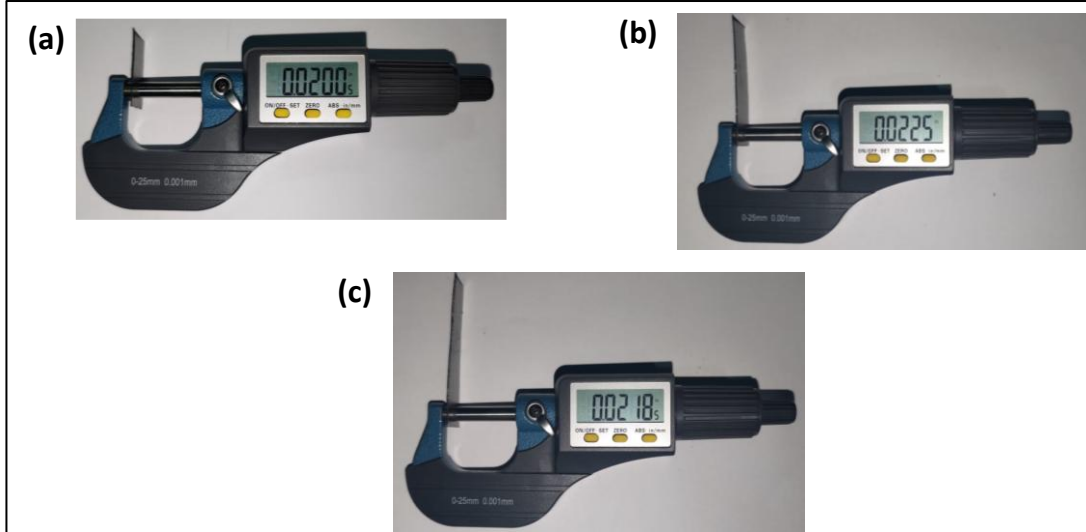


Figure 4.1. Images of graphite sheet electrodes coated with the active material, measured using a digital micrometre: (a) Uncoated graphite sheet. (b) Graphite sheet coated with rGO. (c) Graphite sheet coated with A-7.

Further, the volumetric capacitance (C_V , F cm^{-3}), gravimetric energy density (E_g , Wh kg^{-1}), gravimetric power density (P_g , W kg^{-1}), volumetric energy density (E_V , Wh L^{-1}) and volumetric power density (P_V , W L^{-1}), were calculated according to equations 4.5–4.9 respectively [30]:

$$C_V = C_S \rho \quad (4.5)$$

$$E_g = \frac{1}{2 \times 4} \frac{C_S \times V^2}{3.6} \quad (4.6)$$

$$P_g = \frac{E_g}{\Delta t} \times 3600 \quad (4.7)$$

$$E_V = \frac{1}{2 \times 4} \frac{C_V \times V^2}{3.6} \quad (4.8)$$

$$P_V = \frac{E_V}{\Delta t} \times 3600 \quad (4.9)$$

Where, $\rho (= \frac{m}{V_{el}})$ represents the density of the material and is calculated by dividing the net mass (g) of the electrode by its volume (V_{el} , cm^{-3}). The thickness of the electrode material was measured using a micrometre (Figure 4.1).

4.2.5 Quantification and statistical analysis

The graphs in both the main text and the supplemental file were generated from raw data using OriginPro 2024b (Learning Edition). SEM images were analyzed with ImageJ, and the area under the CV curves was estimated using OriginPro 2024b (Learning Edition) to calculate the specific capacitance. CV, GCD and EIS measurements were performed using a Metrohm Autolab PGSTAT204 instrument (Metrohm Autolab B.V., Netherlands), operated with the NOVA software package (version 2.1.6).

4.3 Results and discussion

4.3.1 Chemical composition analysis

X-ray photoelectron spectroscopy was employed to analyze the chemical composition of the $\text{NH}_2\text{-rGO}$ samples. It is a widely used technique for analyzing the surface chemical structure of graphene, especially in samples that have been chemically modified [42]. The survey spectra of all $\text{NH}_2\text{-rGO}$ samples, shown in Figure 4.2 (a), exhibit C1s, N1s and O1s peaks at binding energies of ~ 284 eV, ~ 399 eV, and ~ 532 eV, respectively. The peak at ~ 399 eV confirms the successful incorporation of nitrogen species into all samples. The atomic concentrations for the samples are depicted in Figure 4.2 (b). The C: O ratios for all the samples are greater than GO ($\sim 1.7:1$) [12], which indicates successful deoxygenation/ reduction during the reaction, aligning with the XRD results. Moreover, this implies that the C: O ratio can be regulated by modifying the pH of the RM during synthesis. Additionally, the nitrogen content can be tuned by controlling the pH of the RM. The nitrogen content increased from 2.48% for A-5 to 5.95% for A-7 and then decreased to 2.98% for A-9 and 1.93% for A-12. Thus, the amination degree is strongly influenced by the pH of the RM, indicating that a highly basic condition is not favourable for amine graft [12]. The diminished ability of ammonia to adsorb onto the graphite sheets in the RM in an

alkaline environment might be the primary cause for the reduced incorporation of nitrogen species [12,43]. Furthermore, in order to differentiate whether the observed nitrogen is connected to graphene through covalent bonds or merely adhered to its surface through physisorption, high-resolution C1s and N1s spectra were recorded and deconvoluted. As shown in Figures 4.3 (a)-(d), the C1s spectrum of all NH₂-rGO samples can be fitted with six components. The component at 284.7 eV is attributed to sp²-bonded carbons in aromatic domains (C=C) [32].

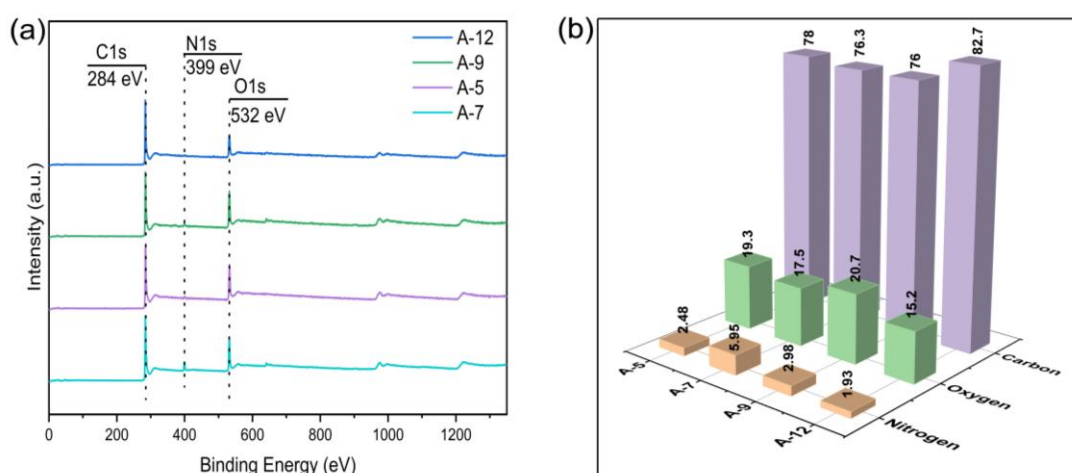


Figure 4.2. XPS survey spectra and atomic concentrations (a) XPS survey spectra of A-5, A-7, A-9 and A-12. (b) Atomic concentrations of A-5, A-7, A-9 and A-12 obtained from XPS.

The remaining three peaks at 289.1 eV, 288.2 eV and 286.7 eV are assigned to COOH, C=O and C-OH & C-O-C groups, respectively [12,44–46]. Additionally, the component at 285.8 eV in all the samples is attributed to the existence of C-N groups, indicating successful amination [12,44]. The last peak, around 291 eV, is assigned to the $\pi - \pi^*$ shakeup satellite of the C=C peak [32].

The N1s spectrum of A-7 (Figure 4.4 (b)) can be deconvoluted into three components with binding energies of 399.8 eV, 401.4 eV and 403.8 eV, corresponding to primary amines[47,48], graphitic-N and pyridinic-O respectively [32]. The spectrum indicates that amine functionality is the predominant nitrogen species, accounting for 81.32% of the peak area, while graphitic and pyridinic nitrogen species are present in much

smaller amounts, at 15.28% and 3.40%, respectively. Similarly, the N1s spectra of A-5, A-9, and A-12 were also deconvoluted as shown in Figures 4.4 (a), (c) and (d) respectively.

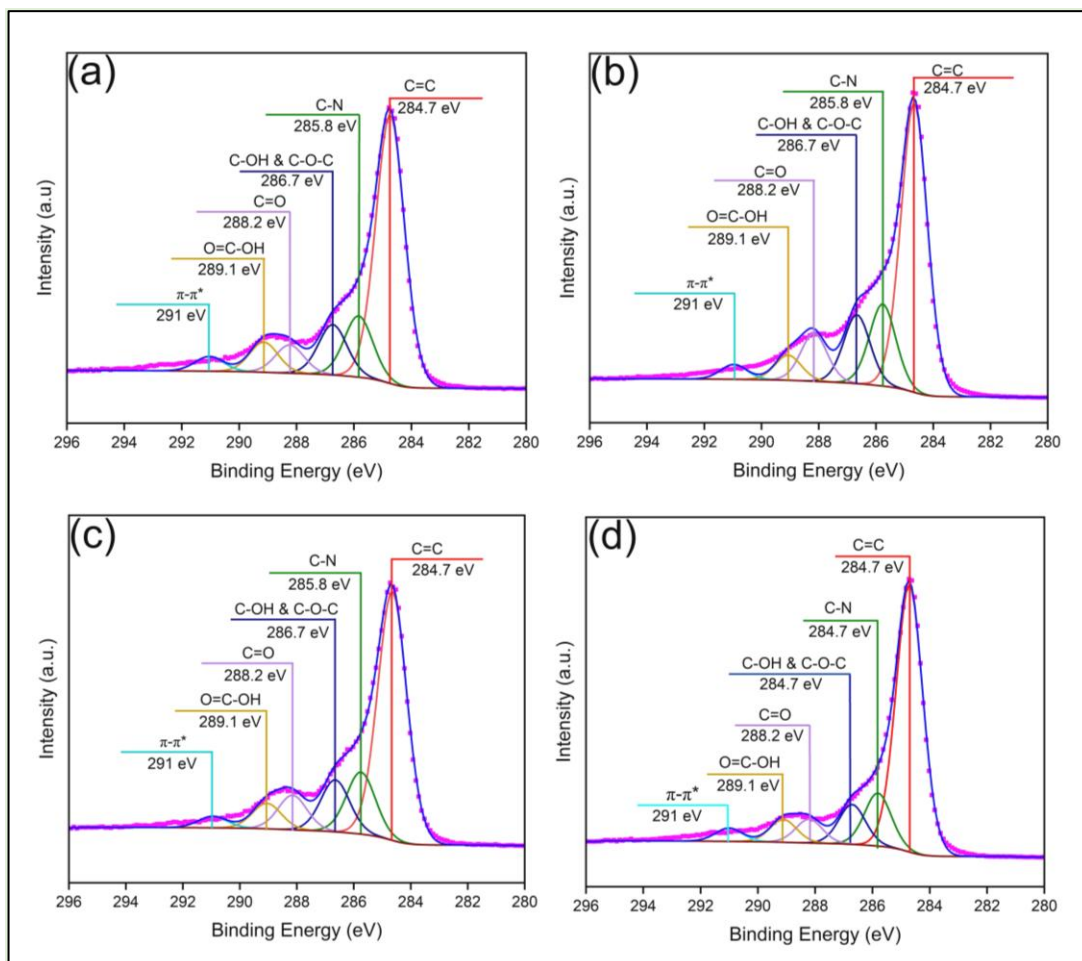


Figure 4.3. Deconvoluted HR-XPS spectra of C 1s region of (a) A-5, (b) A-7, (c) A-9, (d) A-12.

It was observed that their N1s spectrum could be broken down into four components: pyridinic-N (398.4 eV), primary amines (399.8 eV), graphitic-N (401.4 eV), and pyridinic-O (403.8 eV). Notably, all the deconvoluted spectra exhibited peaks at 399.8 eV and 401.4 eV corresponding to primary amines and N–C bonds.

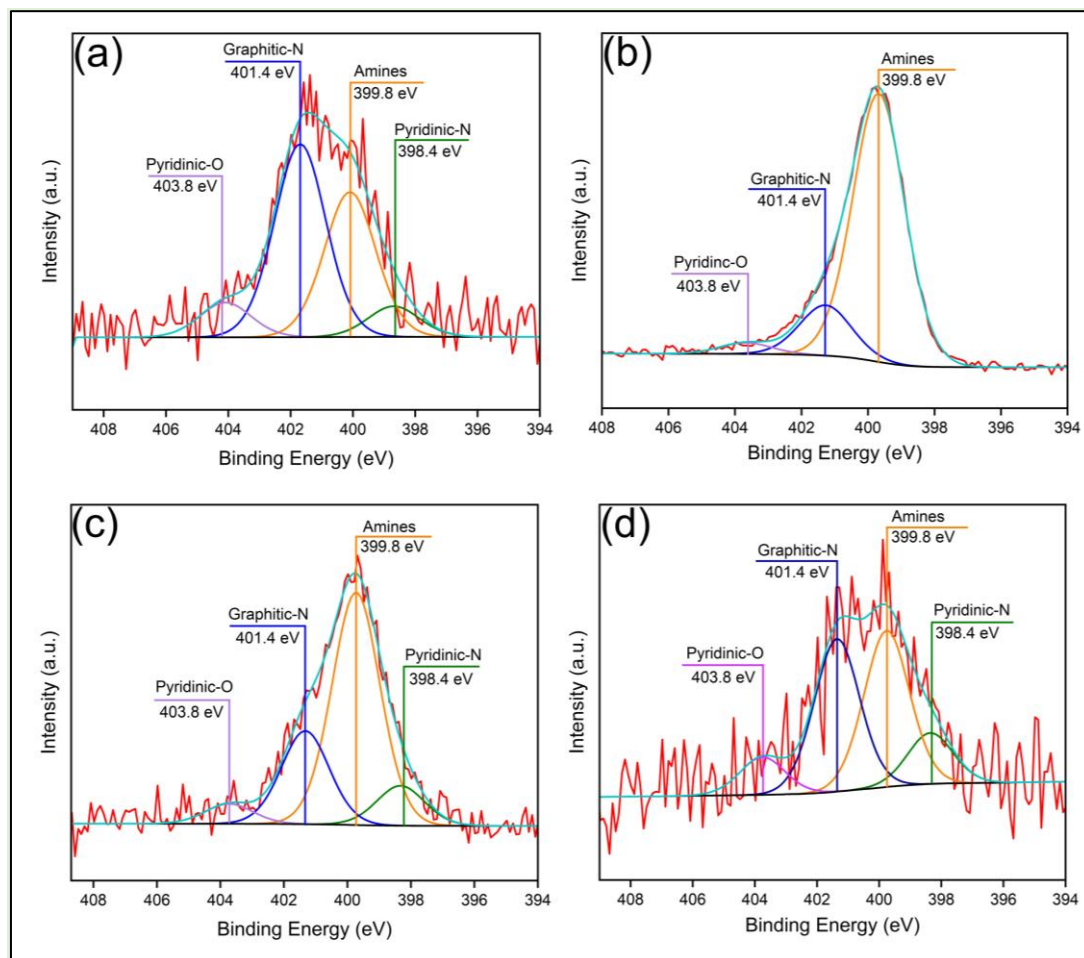


Figure 4.4. Deconvoluted HR-XPS spectra of N 1s region of a) A-5, (b) A-7, (c) A-9, (d) A-12.

This indicates the formation of chemical bonds between the nitrogen from the amines and the carbon framework, confirming the actual functionalization of the graphene structures [49]. Table 4.1 summarizes the concentrations of functional groups obtained by deconvoluting the N1s and C1s spectra of A-5, A-7, A-9 and A-12.

Table 4.1: The relative concentrations of some of the functional groups determined by deconvoluted HR-XPS spectra of N 1s and C 1s regions of NH₂-rGO samples.

Component	C=C	C-N	C-OH & C-O-C	C=O	O=C-OH	Pyridinic-N	Primary Amines	Graphitic-N	Pyridinic-O
Binding energy (eV)	284.7	285.8	286.7	288.2	289.1	398.4	399.8	401.4	403.8
A-5	61.08	13.99	11.48	6.38	7.01	7.60	35.93	47.85	8.61
A-7	54.77	15.55	13.05	9.08	4.75	0.00	81.32	15.28	3.40
A-9	57.26	14.28	11.96	7.97	5.87	10.36	60.28	24.19	5.18
A-12	63.60	12.62	9.49	5.66	5.44	12.82	39.31	38.39	9.48

The successful amination is also demonstrated through FTIR spectroscopy. The FTIR spectra of all samples are illustrated in Figure 4.5 (a) and (b). The bands at 1400 cm^{-1} , 1622 cm^{-1} , and 1732 cm^{-1} can be attributed to C–H/ C–H₂ vibrations and C=O in carbonyl and carboxylic acid moieties [44–46,50]. Additionally, in all samples, the characteristic bands of GO at 1220 cm^{-1} , 1365 cm^{-1} , and 2970 cm^{-1} associated with oxygen functionalities and interlayer water either disappear or decrease, indicating successful dehydration and reduction. Moreover, a peak centred at $\sim 3440\text{ cm}^{-1}$, along with peaks at 1580 cm^{-1} and 1064 cm^{-1} attributed to N–H stretching, N–H bending and C–N stretching of primary amines, is observed [32]. This indicates successful amination, which aligns with the XPS results.

4.3.2 Study of the morphological features

The structural characteristics of the synthesized NH₂–rGOs were further examined using various techniques, including X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD spectra were measured over a 2θ range (5° – 60°) with a scan rate of 0.02° . As shown in Figure 4.5 (c), the spectra reveal a (002) diffraction peak around $2\theta \approx 25^\circ$ corresponding to an interlayer spacing of 0.35 nm. This suggests effective reduction and partial disruption of the long-range order typical of graphite, as well as a change in the distance between layers. This disruption is attributed to the incorporation of amino groups during the reduction process, which alters the stacking arrangement of the graphene layers [51]. Additionally, the spectra display a (10) diffraction peak at $2\theta \approx 45^\circ$, indicating the presence of short-range order [47,52]. Importantly, the XRD pattern of all NH₂–rGO samples lacks the characteristic features of GO. This absence of GO peaks indicates the successful reduction of functional groups containing oxygen, such as epoxy and hydroxyl groups. These results align with the findings from XPS and FTIR findings. In contrast, the solvothermal process developed by Lai and Colleagues [12] retains GO features post-reduction suggesting a less complete reduction compared to the present method. This highlights the effectiveness of the current method.

The morphology and elemental composition of the NH₂–rGO samples were also analyzed using SEM and energy dispersive spectroscopy (EDS). The SEM images of

A-5, A-7, A-9, and A-12 are presented in Figures 4.6 (a)-(d). The Figures reveal that the NH_2 -rGO samples are composed of thin sheets that are haphazardly clustered together, forming a wrinkled and twisted structure characteristic of graphene-based materials. This indicates that the applied synthesis method had no significant effect on the morphology [53]. The distribution of nitrogen, oxygen and carbon in all samples was also quantified by SEM-EDS (Table 4.2). The elemental composition analysis showed significant variation in nitrogen concentration across the samples, with A-7 having the highest nitrogen content (5.01%), followed by A-9 (2.46%), A-5 (2.26%), and A-12 (0.33%).

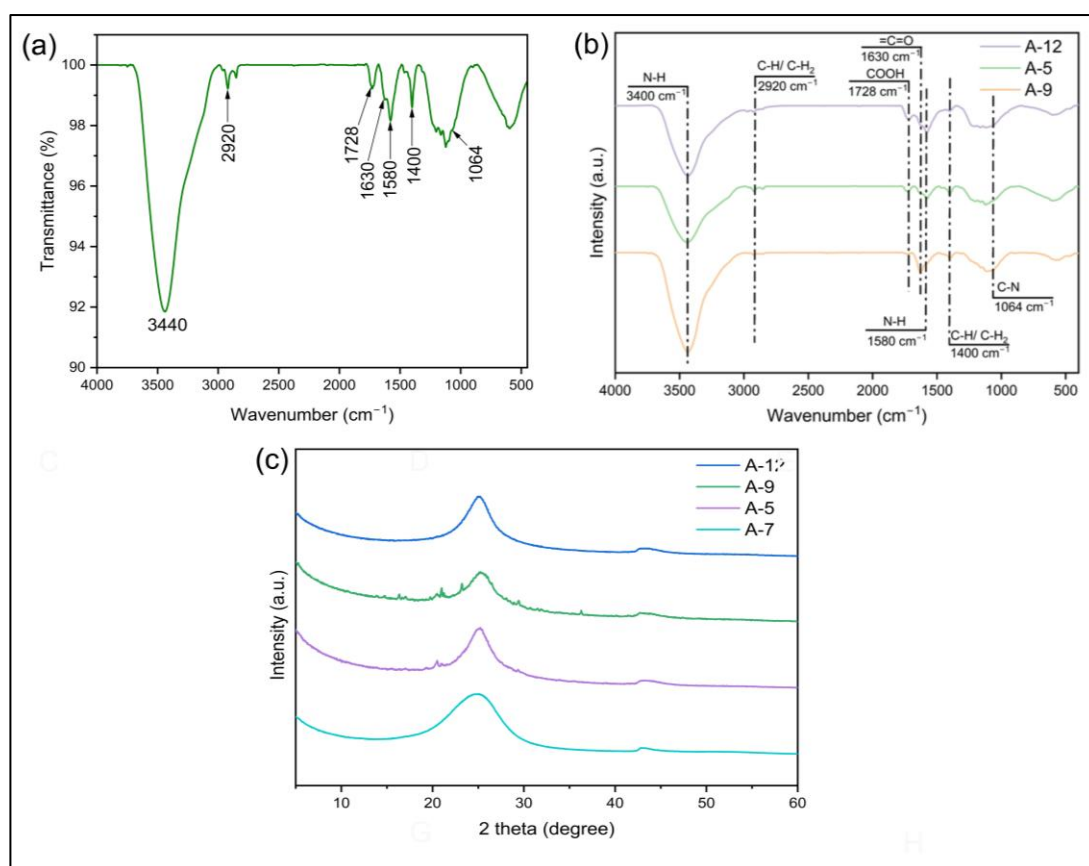
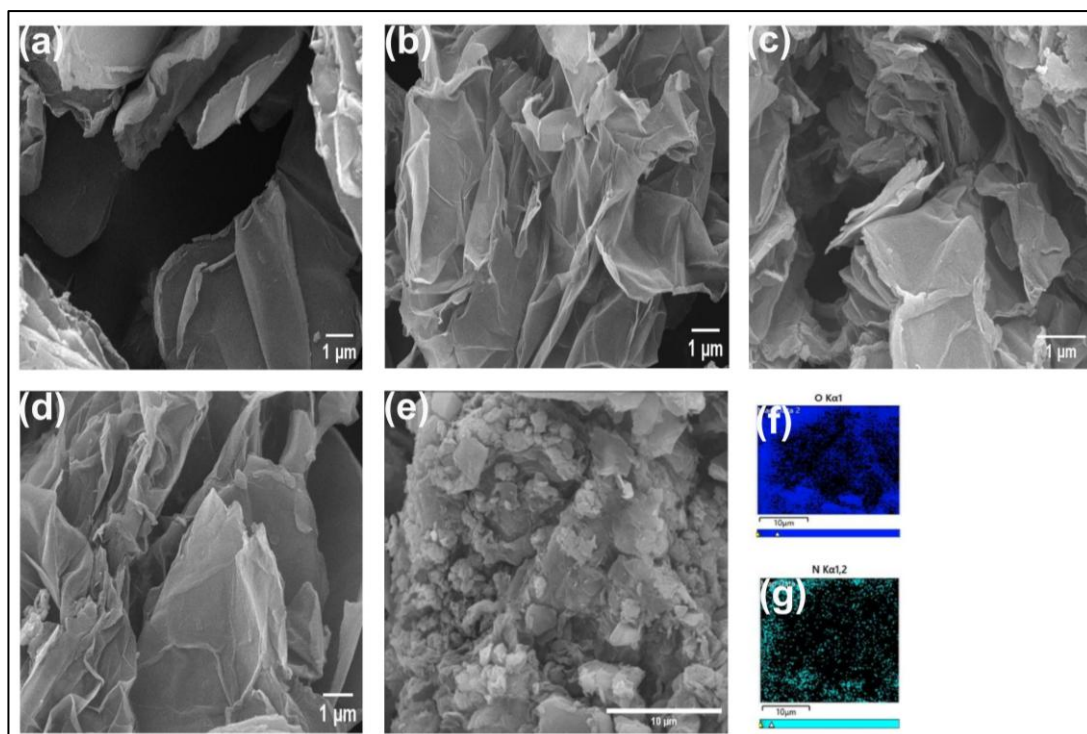


Figure 4.5. (a) FTIR spectrum of A-7. (b) FTIR spectrum of A-5, A-9 and A-12. (c) XRD spectra of A-5, A-7, A-9 and A-12.

These findings align with the XPS results, which display the same trend. Since A-7 has the highest nitrogen content, element distribution mapping was conducted to examine the distribution of different elements throughout the matrix, as depicted in

Figure 4.6 (e)-(g). The results reveal that nitrogen is uniformly and densely distributed across the carbon matrix, demonstrating that the reaction occurred at both the edges and within the bulk of the matrix. Therefore, the present reported method offers several benefits, including simplicity, cost-effectiveness, reduced reaction time, and



high yield, in comparison to other techniques reported in the literature [12,32].

Figure 4.6. FE-SEM image of (a) A-5 (b) A-7 (c) A-9 and (d) A-12. Scale bars, 1 μm . (e) SEM image of A-7 utilized for elemental mapping, including (f) oxygen map, (g) nitrogen map.

Table 4.2: Concentration of elements (in at.%) according to EDS.

Sample	Carbon	Oxygen	Nitrogen	Other Elements
A-5	81.32	2.05	2.05	Sodium (0.11 at %)
A-7	74.82	18.78	5.01	Sulphur (1.39 at %)
A-9	82.58	14.95	2.46	Sodium (0.02 at %)
A-12	86.98	12.69	0.33	--

4.3.3 Electrochemical Performance

Graphene and its composites have recently emerged as promising alternatives to traditional carbon electrodes in supercapacitor applications, offering improved performance [51,54,55]. Therefore, considering the potential of $\text{NH}_2\text{-rGO}$ as an electrode material, we investigated its application in supercapacitors. The electrochemical performance of $\text{NH}_2\text{-rGO}$ samples, along with rGO as a control material, was initially assessed in a three-electrode cell. Figure 4.7 (a) shows the CV curves of all the samples within the potential range of -0.6 to 1.2 V at 5 mV s^{-1} versus Ag/Ag^+ .

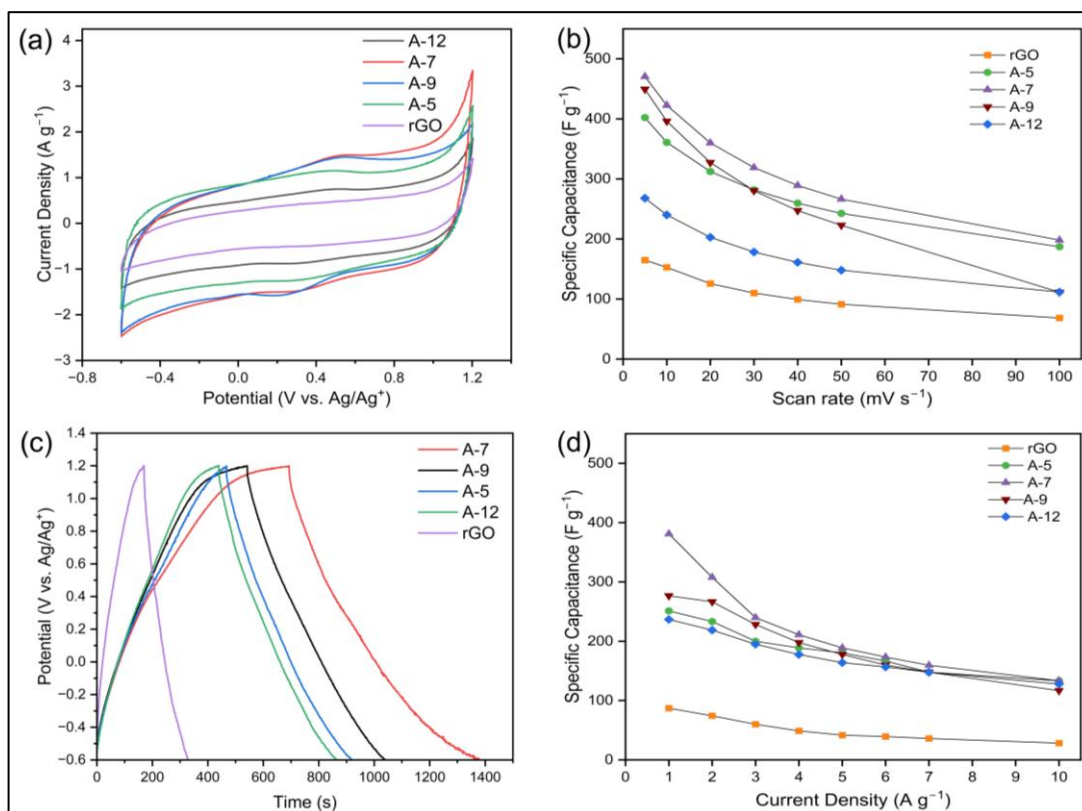


Figure 4.7. Electrochemical properties of $\text{NH}_2\text{-rGO}$ and rGO in 1 M EMIMBF₄ electrolyte in three-electrode configuration (a) CV curves at 5 mV s^{-1} . (b) Variation of C_s with scan rate. (c) GCD curves at 1 A g^{-1} . (d) Variation of C_s with current density.

The CV profiles exhibit a rectangular shape characteristic of electric double-layer capacitance (EDLC), with minor redox peaks likely resulting from the nitrogen and

oxygen functional groups present, as confirmed by XPS and FTIR analyses [30,54]. Among the samples, A-7 demonstrates the largest enclosed CV area, signifying superior energy storage capability compared to A-5, A-9, A-12, and rGO. The similar CV areas of A-5 and A-9 correlate with their comparable nitrogen content, as determined by XPS and EDS analyses. Meanwhile, A-12, which contains the lowest nitrogen content, exhibits the smallest CV area among the NH₂-rGO samples.

All electrodes exhibited the highest specific capacitance (C_s) at 5 mV s⁻¹ and showed a steady decrease as the scan rate increased, which is generally anticipated because of diffusion limitations within the electrode surface's pores (Figure 4.7 (b)) [56]. Notably, A-5, A-7, A-9, and A-12 exhibit capacitance values that are 2.43, 2.85, 2.72, and 1.62 times higher than rGO, highlighting their superior performance. The enhanced performance of NH₂-rGO can be credited to an enhanced ion-accessible surface area, which facilitates better diffusion of ions and quicker ion extraction/insertion [51,57]. To further evaluate the performance of the electrode materials, GCD (galvanostatic charge-discharge) measurements were conducted at various current densities ranging from 1 to 10 A g⁻¹. Figure 4.7 (c) presents the GCD profiles of all the samples at 1 A g⁻¹, which are quasi-triangular in shape, indicating predominantly capacitive behaviour. The specific capacitance (C_s) values were calculated from the GCD curves using equation (2). At 1 A g⁻¹, the C_s values were 1150.20 F g⁻¹, 1573.2 F g⁻¹, 1229.4 F g⁻¹, 894.60 F g⁻¹ and 345.60 F g⁻¹ for A-5, A-7, A-9, A-12 and rGO respectively. Additionally, the variation of C_s with current density is depicted in Figure 4.7 (d). There is a noticeable drop in C_s at lower current densities, followed by a more gradual decline at higher current densities, highlighting the enhanced power capability of NH₂-rGOs. This decrease is likely attributed to reduced ion accessibility to the active surface at higher current densities [56]. Remarkably, A-7 retained a specific capacitance of 432 F g⁻¹ at 10 A g⁻¹, nearly five times greater than that of rGO, as shown in Figure 4.7 (d). The results indicate a clear trend: as the nitrogen content increases, the electrochemical performance improves, with A-7 emerging as the best-performing electrode, followed by A-9, A-5, and A-12. Thus, the results highlight the potential of NH₂-rGOs, particularly A-7 as an advanced electrode for supercapacitors.

Its superior performance is due to the presence of nitrogen species that improve the surface wettability thereby aiding ion transport across the surface.

To investigate the practical applications of $\text{NH}_2\text{-rGO}$, symmetric two-electrode supercapacitor devices were fabricated and tested. Based on its superior performance in the three-electrode system, A-7 was selected as the active material for the symmetric supercapacitor.

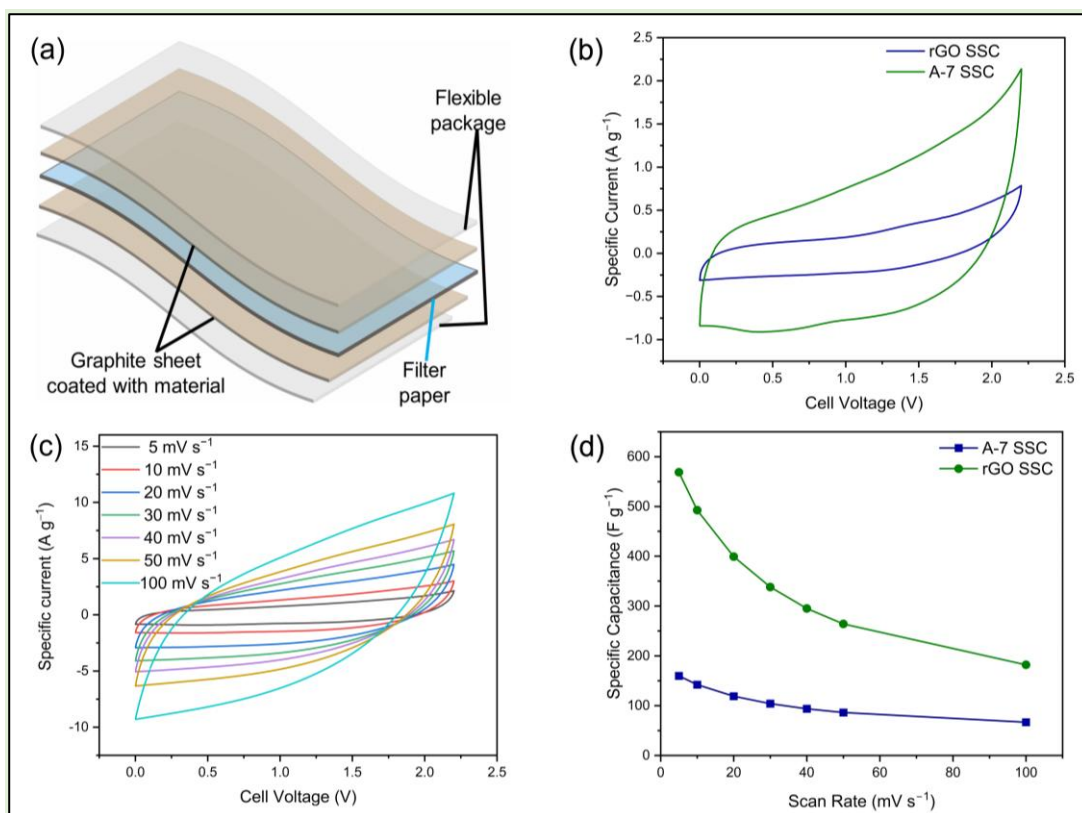


Figure 4.8. Schematic representation and electrochemical performance of the symmetric supercapacitors (a) Schematic representation of fabrication of symmetric supercapacitor device. (b) CV curves at a scan rate of 5 mV s⁻¹. (c) CV of A-7 SSC at different scan rates. (d) CS of the devices at different scan rates.

Two pieces of graphite sheets of dimensions (length=3 cm, width=1cm, thickness=200 microns) were coated with the active material in a 1 cm × 1 cm area. The coated sheets were separated by grade 1 Whatmann filter paper, which was soaked in 1 M EMIMBF₄ in acetonitrile overnight before the fabrication of the device (Figure 4.8 (a)). For

comparison, a symmetric supercapacitor using rGO as the active material was fabricated under identical conditions. These devices were then subjected to performance evaluations to assess their potential for practical applications.

Figure 4.8 (b) demonstrates the CV curves at a scan rate of 5 mV s^{-1} of the assembled supercapacitors within the 0 to 2.2 V potential window. It can be observed that the CV curves show a rectangular shape, typical of EDLC behaviour [30,58]. Further, the rectangular shape was preserved even at scan rates of 100 mV s^{-1} (Figure 4.8 (c)) for A-7 based symmetric supercapacitor (A-7 SSC), which is an indication that the symmetric supercapacitor demonstrates capacitive behaviour with rapid charge transport at the interfaces as well as the material [59]. The C_s computed from the CV curves at different scan rates are presented in Figure 4.8 (d).

A-7 demonstrated a C_s of 568.69 F g^{-1} at 5 mV s^{-1} , which is a 3.5-fold increase as compared to rGO-based symmetric supercapacitor (rGO SSC) and at 100 mV s^{-1} , A-7 SSC delivered a C_s of 182.10 F g^{-1} , further highlighting the ease of ion access throughout the entire architecture. GCD measurements were conducted to evaluate the electrochemical performance of the fabricated supercapacitor devices. Figure 4.9 (a) illustrates the GCD curves of rGO SSC and A-7 SSC at 1 A g^{-1} . Both curves exhibit a triangular profile, indicative of capacitive energy storage behaviour, consistent with the trends observed in the CV analysis. Notably, A-7 SSC demonstrated a specific capacitance (C_s) of 322 F g^{-1} at 1 A g^{-1} , representing a five-fold improvement over rGO SSC (Figure 4.9 (b)). This value is greater than those of N-doped graphene (205.3 F g^{-1} at 1 A g^{-1}), rGO (133 F g^{-1} at 1 A g^{-1}) [28], N-modified few-layer graphene (227 F g^{-1} at 1 A g^{-1}) [30], flame-induced rGO (260 F g^{-1} at 0.1 A g^{-1}) [60], porous graphene framework (237 F g^{-1} at 0.2 A g^{-1}) [54], holey graphene framework (298 F g^{-1} at 1 A g^{-1}) [61] and is among the highest reported for supercapacitors based on graphene (Table 4.3). Additionally, A-7 SSC demonstrated its superiority in both gravimetric and volumetric terms. These metrics are critical in the portable energy storage market, where the simultaneous optimization of energy and power density is highly valued [41,62–64]. Energy density determines the overall energy storage capacity, while high power density allows for rapid charging/discharging. Although

supercapacitors excel in providing high power densities, their energy density remains a significant limitation that needs improvement.

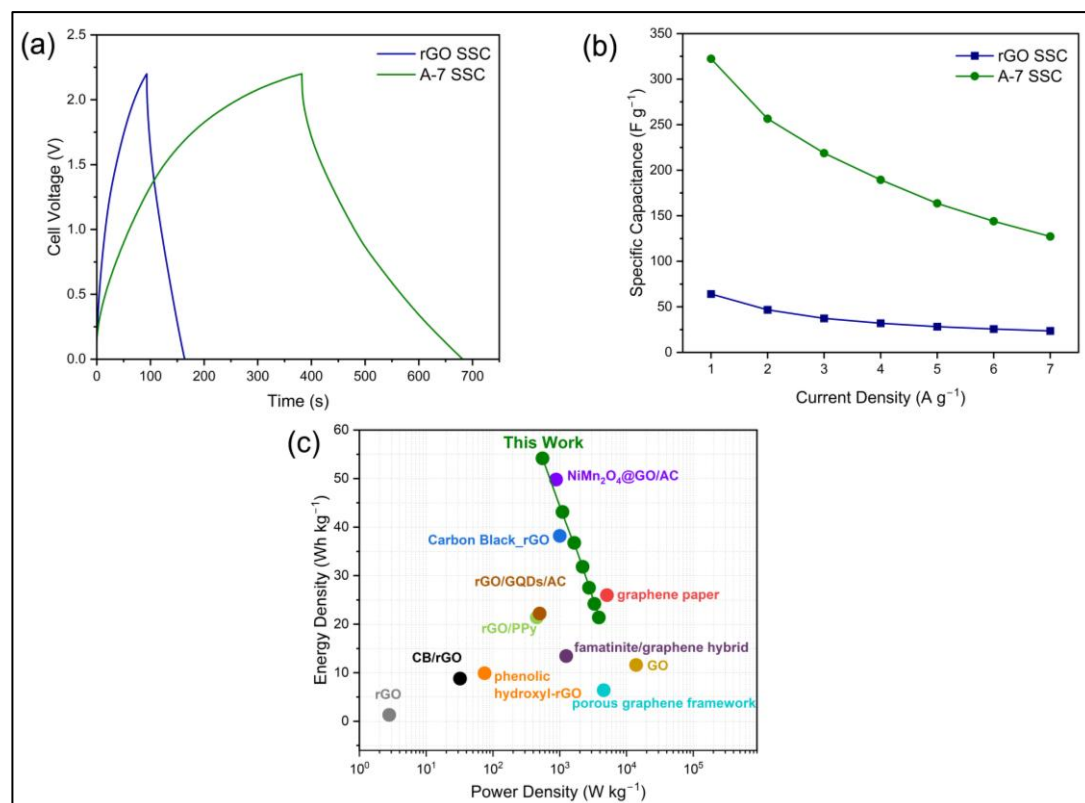


Figure 4.9. Electrochemical performance of the symmetric supercapacitors (a) GCD curves of the devices at 1 A g⁻¹. (b) C_s of the devices at different current densities. (c) Ragone plot.

A-7 SSC displayed an impressive gravimetric energy density of 54.18 Wh kg⁻¹ at 1 A g⁻¹, five times higher than rGO SSC (10.77 Wh kg⁻¹ at 1 A g⁻¹). A-7 SSC also demonstrated a volumetric energy density of 48.16 Wh L⁻¹ at 1 A g⁻¹ which is almost seven times as compared to rGO SSC (6.89 Wh L⁻¹). Moreover, at a current density of 7 A g⁻¹, the gravimetric and volumetric energy densities for A-7 SSC remained high at 21.39 Wh kg⁻¹ and 19.01 Wh L⁻¹, while the volumetric and gravimetric power densities increased to 3422.22 W L⁻¹ and 3850 W kg⁻¹ respectively indicating much-enhanced performance. The Ragone plot in Figure 4.9 (c) shows that the A-7 SSC outperforms many graphene-based supercapacitors, even exceeding some binary composites [54,65–74].

Table 4.3: Comparison of specific capacitance of carbon-based materials as supercapacitor electrodes.

Materials	Gravimetric capacitance (F g^{-1})	Current density/ Scan rate	Electrolyte	Ref
High density porous graphene macroform	238	0.1 A g^{-1}	6 M KOH	[75]
S-porous carbon/graphene	109	0.05 A g^{-1}	6 M KOH	[76]
Reduced graphite oxide with high density	182	1 A g^{-1}	6 M KOH	[77]
KOH activated graphene	165	1.4 A g^{-1}	BMIM BF_4/AN	[78]
High density rGO	182	1 A g^{-1}	6 M KOH	[77]
activated microwave-expanded G-O spheres	174	4.2 A g^{-1}	[BMIM][BF_4]/AN	[79]
Holey graphene framework	298	1 A g^{-1}	EMIM BF_4/AN	[61]
Nitrogen-enriched nonporous carbon	115	0.05 A g^{-1}	1 M H_2SO_4	[80]
Seaweed biopolymer-derived carbon	198	2 mV s^{-1}	1 M H_2SO_4	[81]
Copper nanocrystal-modified activated carbon	79	0.2 A g^{-1}	TEATFB	[82]
rGO	255	0.5 A g^{-1}	6 M KOH	[83]
3D nitrogen and boron co-doped graphene	239	1 A g^{-1}	1 M H_2SO_4	[84]
3D N-doped graphene-CNT	180	0.5 A g^{-1}	6 M KOH	[85]
B-doped graphene nanoplatelets	160	1 A g^{-1}	6 M KOH	[86]
N-doped graphene sponge	286.86	5 mV s^{-1}	1 M NaCl	[87]
3D porous carbon	226	1 mV s^{-1}	1 M H_2SO_4	[88]
Graphene-cellulose paper	120	1 mV s^{-1}	1 M H_2SO_4	[89]
Graphene/Polyaniline Composite Paper	233	---	1 M H_2SO_4	[90]
NH_2 -rGO	322	1 A g^{-1}	1 M EMIM BF_4/ACN	Present work

Electrochemical impedance spectroscopy (EIS) tests were also performed to gain deeper insights into the capacitive behavior of the devices. Figure 4.10 (a) presents the Nyquist plot comparisons for the devices. At high frequencies, the impedance data shifted from positive to negative, indicating inductive behaviour in this region. This inductance is not related to the electrochemical processes within the supercapacitor but is instead attributed to stray inductance, commonly observed in supercapacitors and battery cells, and is primarily caused by cables and cell connections [91]. It is however important to account for this inductance during the fitting and simulation of experimental impedance data to determine the cell's electrical parameters accurately. The Nyquist plots also revealed a Warburg region and a smaller semicircle, indicating lower charge transfer resistance at the interfaces and the bulk material, which implies efficient electrolyte ion diffusion [92,93]. The plots were fitted utilizing an equivalent circuit (inset of Figure 4.10 (a)), which revealed the equivalent series resistance to be $\sim 12.7 \Omega$ for rGO SSC and 15.5Ω for A-7 SSC. Additionally, the charge transfer resistance was found to be low, at 2.05Ω for rGO SSC and 2.03Ω for A-7 SSC. The nearly vertical slope in the low-frequency region indicates highly capacitive behaviour, which is in agreement with CV and GCD analysis.

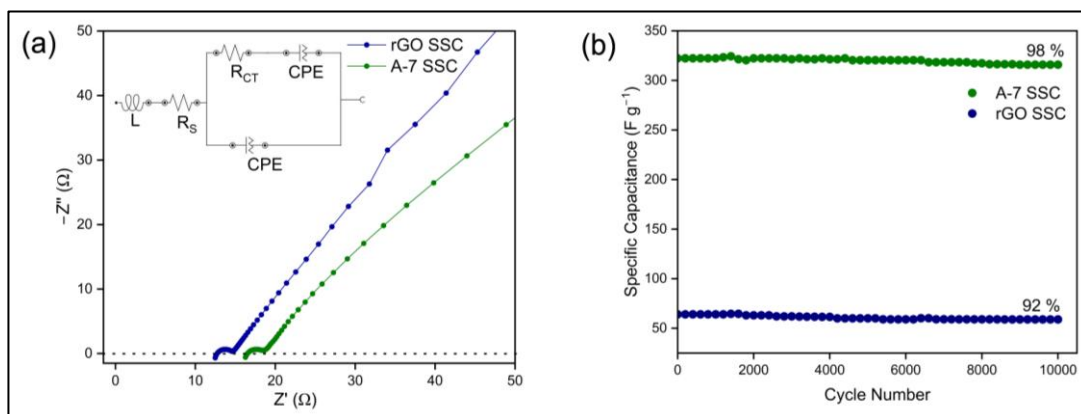


Figure 4.10. (a) Nyquist plots of A-7 SSC & rGO SSC (inset is the circuits used for fitting of EIS curves). (b) Cycling stability of A-7 SSC and rGO SSC at $7 A g^{-1}$.

Cycling stability is another crucial factor for practical applications. Figure 4.10 (b) illustrates the cycling stability of A-7 SSC and rGO SSC, determined through a GCD test at $7 A g^{-1}$. A-7 SSC shows a 98% capacitance retention after 10,000 cycles, compared to 92% for rGO SSC, indicating its excellent cyclability. For comparison,

the reported capacitance retention of some high-performance graphene-based electrodes is 96.5 % after 10,000 cycles for laser-scribed graphene electrochemical capacitors [94], 57% for capillary-densified graphene [95], 97% for porous graphene frameworks [54], 77 % for polyoxometalate/rGO [96], 79% for graphene/polyaniline nanofiber [97], 90.3 % for N-doped graphene [29], <90 % for thermal reduced GO [98]. These comparisons underscore the exceptional charge transport capabilities of $\text{NH}_2\text{-rGO}$ and its promising potential for use as supercapacitor electrodes.

4.4 Conclusion

In conclusion, we have demonstrated a simple and scalable method for synthesizing aminated reduced graphene oxide in a single step. This is currently one of the fastest synthesis methods available for this material, with the entire process completed in approximately 9 hours. The nitrogen content can be adjusted by varying the pH of the reaction mixture, with ammonia serving as the nitrogen source. XPS and FTIR analyses validate the presence of primary amines in the graphene. This method facilitates the reduction of graphene and the introduction of up to 6 atomic % of amines, with the XPS data indicating a minimal presence of other nitrogen species, such as pyridines. Elemental mapping reveals a uniform distribution of nitrogen throughout the $\text{NH}_2\text{-rGO}$ matrix. The $\text{NH}_2\text{-rGO}$ exhibited enhanced electrochemical performance compared to rGO, including a high specific capacitance in three-electrode configuration and symmetric supercapacitor devices. Specifically, A-7 SSC achieved the highest C_s of 322 F g^{-1} at a current density of 1 A g^{-1} , which is a fivefold increase compared to rGO SSC.

Additionally, A-7 SSC demonstrated an impressive gravimetric energy density of 54.18 Wh kg^{-1} at 1 A g^{-1} , five times greater than rGO SSC (10.77 Wh kg^{-1} at 1 A g^{-1}) and a volumetric energy density of 48.16 Wh L^{-1} at 1 A g^{-1} , nearly seven times higher than rGO SSC (6.89 Wh L^{-1}). The enhanced electrochemical performance of $\text{NH}_2\text{-rGO}$ is attributed to improved wettability due to the introduction of nitrogen groups. This method provides a promising strategy for developing advanced high-performance energy storage systems based on graphene. Moreover, this approach could be adapted for post-synthesis modifications or activation of carbon

nanomaterials, offering significant potential in catalysis, biosensors, and energy storage applications.

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Chapter 5

Section-I

Ultrafast, green synthesis of bromographene for high-energy supercapacitors

Section-II

A comparative study on the bromination of reduced graphene oxide using different tribromides

CHAPTER 5

Ultrafast, green synthesis of bromographene for high-energy supercapacitors

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A comparative study on the bromination of reduced graphene oxide using different tribromides

5.1 Overview

This chapter is divided into two interconnected sections. The first section describes the development of a rapid and green synthetic route for bromographene via tribromide-mediated bromination of rGO under reflux for a short reaction duration. The structural, compositional, and electrochemical properties of the synthesized bromographene are investigated, and its performance in a symmetric supercapacitor configuration is evaluated.

The second section extends this study by systematically comparing five different quaternary ammonium tribromides to assess their bromination efficacy toward rGO. Detailed spectroscopic and structural analyses are performed to determine bromine incorporation levels and associated functionalization effects. This comparative investigation provides deeper insight into reagent-dependent bromination efficiency and establishes optimized pathways for designing functionalized graphene derivatives.

Section-I

Ultrafast, green synthesis of bromographene for high-energy supercapacitors

5.2 Introduction

Halogenation of carbon-based materials represents a valuable method for generating highly reactive species that can be utilized in subsequent reactions [1–3]. In particular, modifying graphene, a 2D sheet of sp^2 hybridised carbon atoms, with halogens can allow tailoring its properties such as reactivity, electronic structure and structural alterations. For instance, fluorographene exhibits a band-gap width of approximately 3.4 eV [4]. This is particularly significant because pristine graphene, being a zero band-gap semiconductor, has limited applications in electronics. The most studied halogenated graphene derivative is fluorinated graphene, often referred to as fluorographene [5,6]. However, the robust F–C bond limits its feasibility for chemical modifications [7]. Research on graphene modified with other halogens is much less common. The larger size and lower reactivity of heavier halogens make the synthesis of chloro-, bromo-, and especially iodographenes more difficult. Interestingly, heavier halogens, unlike fluorine and chlorine, have been found to enhance the electrical conductivity of halogen-modified graphenes. Moreover, unlike fluorine, which tends to decrease thermal stability, heavier halogens generally enhance this property [4].

In this context, bromine derivatives of graphene (bromographene) is particularly appealing as a synthetic tool owing to their high reactivity [1–3]. Nevertheless, it is surprising that only a limited amount of research has been conducted on the synthesis of bromographene [8–12]. However, forming a direct covalent bond between bromine and graphene is extremely difficult and typically necessitates harsh methodologies such as plasma treatment [13], microwave treatment [1], or refluxing in bromine [11] thereby making these procedures intricate and typically result in low yields and/or subpar bromination. For instance, Jankovský et al. [7] described bromination of

graphite oxide using bromine and hydrobromic acid at elevated temperature and pressure, achieving a bromine content of 2.7 atomic % as confirmed by XPS analysis. In a separate study, the same group [14], brominated graphene oxide by employing Hunsdiecker reaction. The bromination involved two stages. Firstly, a silver modified graphene oxide was prepared which was subsequently refluxed with bromine for 24 hours under argon atmosphere. This approach resulted in a bromine content of 2.5 atomic % according to XPS analysis. In another study, Au and colleagues [15] synthesized brominated few-layer graphene using liquid bromine through a multi-step process. This method required a low temperature (0 °C), a controlled atmosphere (argon, nitrogen, or vacuum), and high pressure, taking several days to finish. XPS analysis showed that only 0.9 atomic % bromine was incorporated into the graphene structure. Nevertheless, the methods described in literature for preparing bromographene is associated with risks and toxicity concerns, making it a potentially hazardous process. While bromine serves as an efficient reagent, its utilization is constrained by safety risks associated with handling bromine. Additionally, the low bromine content remains a major drawback, and the reaction times often range from several hours to days. Thus, there exists a need in the state of the art to develop a process for preparing bromographene using hazard-free material that enables high bromine incorporation.

Thus, the present study aims to synthesize bromographene using a safer and more environmentally friendly brominating agent while conducting the transformation under moderate temperature and pressure conditions. A key objective in this process is to identify a non-toxic brominating agent wherein, a greener alternative such as tetrabutylammonium tribromide (TBATB) proves to be a superior option. Therefore, this research introduces a novel approach that employs this eco-friendly, mild, and versatile brominating agent, effectively overcoming the drawbacks of previous approaches.

Herein, bromographene with varying bromine concentrations are successfully prepared via a facile one-step method (see Materials and methods for detailed information). Experimental results demonstrate that adjusting the TBATB-to-rGO ratio allows effective control over bromine incorporation, with XPS analysis confirming a bromine content as high as 4.73 %. This constitutes one of the highest levels of bromination reported to date. Notably, this is the first report demonstrating that reduced graphene oxide can be brominated using a tribromide (TBATB), marking a departure from the conventional use of graphene oxide in such reactions. Furthermore, bromination is accomplished within 60 minutes, marking the shortest reported duration to date, in contrast to other literature reports that commonly necessitate several hours [9,11,12]. Moreover, the incorporation of bromine may improve the wettability of brominated graphene, enhancing its potential for electrochemical applications.

A systematic investigation was conducted to determine how the functionalization influences the potential of bromographene as an electrode material for supercapacitor, demonstrating significant performance enhancements. A symmetric supercapacitor assembled with the synthesized material exhibited elevated specific capacitance and remarkable improvements in gravimetric energy densities, outperforming non-brominated rGO by several folds and even exceeding the performance of some binary/ternary composites. Furthermore, the use of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) helped expand the operating voltage window to 3.5 V, significantly boosting the material's suitability for real-world energy storage applications. Moreover, bromographene may act as a versatile precursor for the synthesis of a wide range of functionalized derivatives of graphene and subsequent chemical modifications, thereby extending its applicability across diverse fields. Additionally, the developed method holds potential for adaptation to the bromination of other carbon materials.

5.2.1 Materials and methods

Chemicals and materials

Graphite ($< 20\ \mu\text{m}$), sulfuric acid (98 %), vanadium pentoxide (99.9 %) and sodium hydroxide pellets were obtained from Sigma-Aldrich. Sodium carbonate (99.5 %), tetrabutylammonium bromide (99 %), potassium bromide (99.5 %), acetonitrile (99 %), sodium nitrate (99 %), potassium permanganate (99 %), L-Ascorbic acid (99.7 %) and acetonitrile (99.5 %) were obtained from Sisco Research Laboratories Pvt. Ltd., India. Hydrogen peroxide (30 %) was purchased from Thermo Fisher Scientific India Pvt. Ltd. The chemicals were used as received and deionized (DI) water (Resistivity $18.2\ \text{M}\Omega\ \text{cm}$ @ $25\ ^\circ\text{C}$) was used during the experiment.

Preparation of reduced graphene oxide

Reduced graphene oxide was prepared employing modified Hummer's method [16] with some minor modifications [17]. A schematic illustration of the synthesis procedure is provided in Figure 5.1 (a). In brief, 1 g of high-purity graphite was introduced into 23 mL of concentrated sulfuric acid under continuous stirring in an ice bath. Thereafter, 6 g of potassium permanganate was gradually introduced and the resulting mixture was maintained at $35\ ^\circ\text{C}$ for 30 minutes. This was followed by six alternating cycles of sonication and stirring, each lasting 10 minutes. Afterward, 70 mL of DI H_2O was added into the mixture, which was then subjected to ultrasonic treatment for an additional 30 minutes. The pH of the mixture was then adjusted to approximately 7 by the gradual addition of 10 M sodium hydroxide solution. Thereafter, 100 mL of a 1 M L-ascorbic acid solution was added, and the mixture was stirred for 30 minutes before being refluxed at $90\ ^\circ\text{C}$ for 1 hour. The black precipitate was thoroughly washed with DI H_2O and acetone, and subsequently dried under vacuum at $60\ ^\circ\text{C}$ to yield rGO.

Preparation of tetrabutylammonium tribromide

Tetrabutylammonium tribromide was synthesized following one of our previously reported methods, where a detailed description of the reagent and its preparation is provided [18]. The overall synthesis strategy is schematically illustrated in Figure 5.1 (b). Briefly, 0.05 g vanadium pentoxide (0.27 mmol) was added to a pre-cooled 250 mL beaker containing 5 mL (44.12 mmol) of 30 % hydrogen peroxide. The reaction was conducted under ice–water bath conditions (0–5 °C) to control the exothermic interaction between V_2O_5 and H_2O_2 . The mixture was stirred until complete dissolution of V_2O_5 , affording a reddish-brown solution. An aqueous solution of 3.7 g potassium bromide (31.09 mmol) and 5 g tetrabutylammonium bromide (15.53 mmol) dissolved in 35 mL of DI water was then introduced, followed by the gradual addition of 50 mL of 1 M sulfuric acid in small portions. The reaction mixture was stirred for an additional 2 h while maintaining the ice–water temperature. The resulting bright yellow microcrystalline product was collected by suction filtration using Whatman No. 1 filter paper and dried in open air. The dried product was subsequently recrystallized from acetonitrile, yielding bright orange crystals. The isolated product was obtained in 7.4 g yield (99.5 %) with a melting point of 75 °C.

Synthesis of bromographene

In a typical experiment (Figure 5.1 (c)), a certain amount of TBATB (250 mg, 1250 mg and 5000 mg) was dissolved in 50 mL of acetonitrile. Subsequently, 250 mg of the synthesized rGO was introduced slowly to the reaction mixture while maintaining constant stirring. Later, the mixture was sonicated for 30 mins, followed by refluxing the solution at 80 °C for 1 hour. The reaction mixture was allowed to cool down naturally to room temperature and was washed multiple times with de-ionised water, ethanol and acetone. The obtained solid was then dried at 60 °C to obtain bromographene. The final samples were designated as BG-1, BG-5, and BG-20 based on the TBATB-to-rGO ratio used.

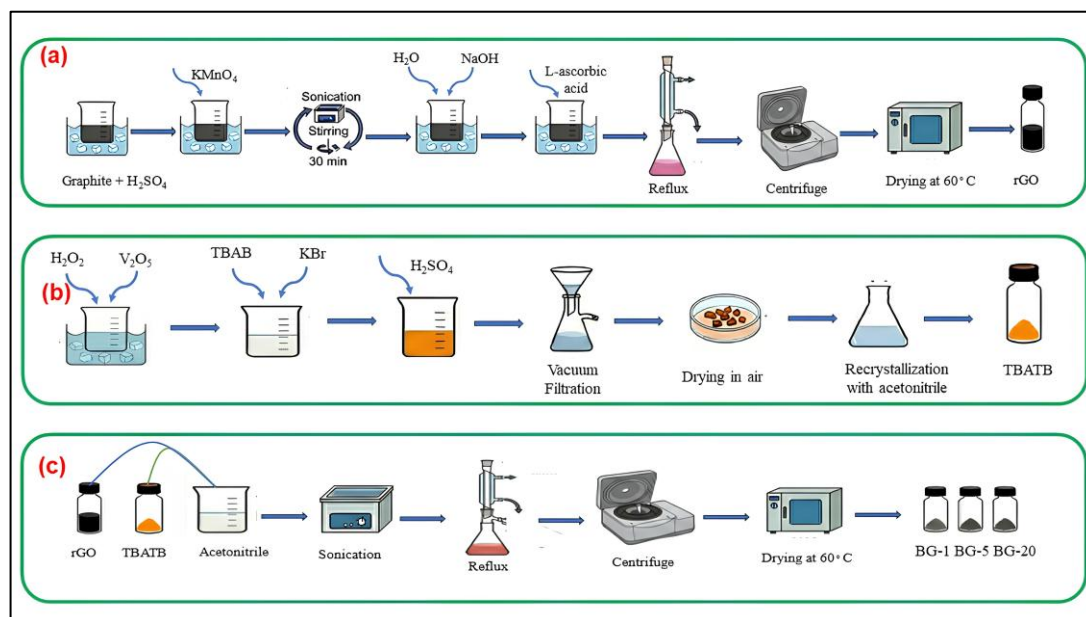


Figure 5.1. Schematic illustration of the preparation of (a) rGO, (b) TBATB, and (c) bromographene.

Materials characterizations

Various analytical techniques were employed to characterize the synthesized bromographenes. Powder XRD patterns were obtained from a Powder X-Ray Diffractometer (Model: X'PertPro, Make: Phillips) using $\text{Cu K}\alpha$ radiation in continuous scanning mode at 40 kV and 40 mA. The functional groups of bromographene samples were characterized by Fourier transform infrared (FT-IR) spectrometer (Model: Spectrum Two, Make: Perkin Elmer) in the range of $4000\text{--}400\text{ cm}^{-1}$ with 1 cm^{-1} resolution. The surface morphology of the samples was investigated using a JEOL JSM 7900F field emission scanning electron microscope (FESEM), and the elemental composition was determined via an energy dispersive X-ray (EDX) detector from Oxford Instruments. The surface elemental composition and chemical bonding nature of bromographene was determined using X-ray photoelectron spectroscopy (Model: Nexsa Surface Analysis System Make: ThermoFisher Scientific). Raman spectra were recorded using an IndiRAM CTR300 micro-Raman spectrometer in the range of $100\text{--}4100\text{ cm}^{-1}$, employing a 532 nm laser with an applied

power of 5 mW and a 50× objective lens. High-resolution transmission electron microscopy (HRTEM) measurements were carried out using an FEI Tecnai G2 20 S-TWIN transmission electron microscope, operating at an accelerating voltage of 200 kV.

Electrochemical measurements and calculations

All electrochemical measurements were conducted using a Metrohm Autolab PGSTAT 204 electrochemical workstation, controlled via the NOVA software package. Electrochemical impedance spectroscopy (EIS) was performed with a 10 mV amplitude over a frequency range of 0.1 Hz to 10 kHz at OCP. The recorded curves were fitted using the NOVA software package (version 2.1.6).

Electrochemical performance was assessed using both two-electrode configuration. The working electrodes were prepared by thoroughly mixing the active material, carbon black, and polyvinylidene fluoride in a weight ratio of 85:5:10 using a mortar and pestle, with N-methyl-2-pyrrolidone serving as the dispersing solvent. The resulting slurry was evenly applied to a 1 cm × 1 cm graphite sheet and subsequently dried under vacuum at 60 °C overnight.

For the symmetric supercapacitor, C_{SP} of a single working electrode ($F\ g^{-1}$) was computed from GCD curves using Equation 5.1 [19,20].

$$C_{SP} = \frac{2(I \times \Delta t)}{m \times V} \quad (5.1)$$

Where, I , Δt , m and V represent the applied discharge current (A), discharge time obtained from GCD curve, the total mass of the material on a single electrode, including the active material, binder, and conductive additive and operating potential window respectively.

Further, gravimetric energy density (E_d , Wh kg^{-1}) and power density (P_d , W kg^{-1}) were determined according to Equations 5.2 and 5.3 respectively [24].

$$E_d = \frac{1}{2 \times 4} \frac{C_{SP} \times V^2}{3.6} \quad (5.2)$$

$$P_d = \frac{E_g}{\Delta t} \times 3600 \quad (5.3)$$

5.2.2 Results and discussion

Surface chemistry characterization

X-ray photoelectron spectroscopy (XPS) was utilized to determine whether bromine atoms were successfully incorporated onto the graphene backbone. XPS is a commonly utilized approach for evaluating the surface chemical structure of graphene, particularly when it has been chemically modified [21]. This method allows for detailed investigation of modifications in the functional groups on the graphene surface and confirms if covalent grafting, such as bromination, has taken place [11]. The wide survey XPS spectrum of all samples is presented in Figure 5.2 (a), where Br 3d, Br 3p, Br 3s, C 1s, N 1s and O 1s peaks are evidently visible. The Br 3d, Br 3p, Br 3s, C 1s, N 1s and O 1s peaks are found at binding energies corresponding to 69 eV, 182 eV, 257 eV, 284 eV, 399 eV and 532 eV, thereby confirming successful bromination. The obtained concentrations of various elements obtained from the XPS analysis are summarized in Table 5.1. A comparison of the bromine content reveals that the degree of bromination achieved through this method is higher than in reports utilizing bromine or hydrobromic acid [9,11,12]. This highlights the efficacy and advantages of this synthesis approach, which enables bromine incorporation in a fraction of the time compared to the extensive processing durations reported in the literature, while also employing a green and environmentally friendly brominating agent [9,11,12].

Table 5.1: Elemental composition of the samples determined from XPS survey spectra, expressed in atomic percent (at %).

Sample	at% C	at% O	at% N	at % Br
BG-1	86.14	12.66	0.77	0.43
BG-5	85.62	9.72	2.49	2.17
BG-20	85.44	5.15	4.68	4.73

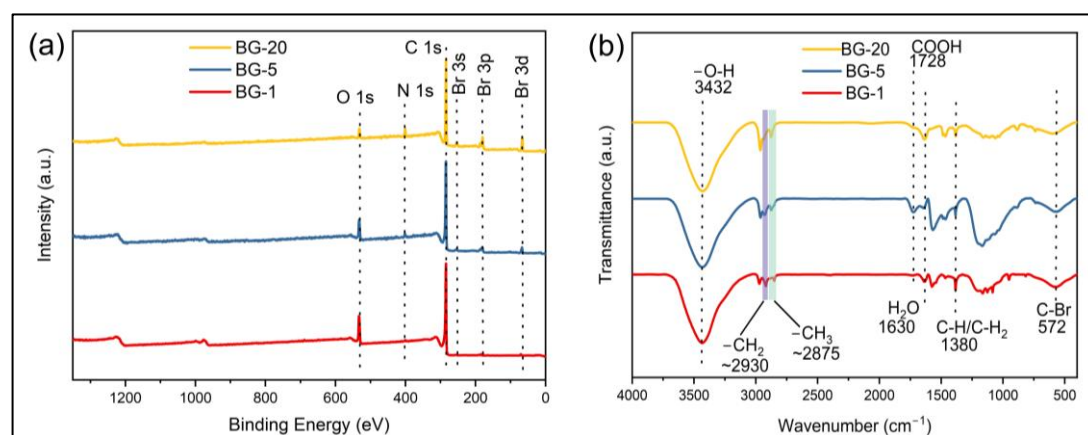


Figure 5.2. XPS survey spectra and FTIR spectra of BG-1, BG-5 and BG-20.

Further, for a comprehensive analysis of the bonding environments of these elements, an in-depth analysis of the Br 3d and C 1s peak was carried out which is depicted in Figure 5.3 (a)–(c) and Figure 5.3 (d)–(f) respectively. For BG-1 and BG-5, the C 1s peak can be deconvoluted into six components, whereas for BG-20, it can be deconvoluted into four components. The component at a binding energy (BE) of 284.4 eV corresponds primarily to non-functionalized sp^2 and sp^3 carbons [22]. It also accounts for non-functionalized sp^2 and sp^3 carbons in the α position of Br, or in the β position of carbonyl or carboxyl groups. Thus, it can be inferred that bromination did not substantially alter the polyaromatic structural units and, consequently, the delocalized π electron systems remain relatively unchanged [23]. The component at a BE of 285.4 eV is attributed to sp^2 carbons covalently bonded to bromine, while the component at a BE of 286.4 eV is associated with carbon atoms participating in

oxygenated groups (C–OH, C–O–C) [9,11,12,22,23]. The components at binding energies of 287.5, 288.8 and 290.3 eV are ascribed to carbonyl (C=O) groups, carboxyl groups and shake up satellite $\pi \rightarrow \pi^*$ respectively [12,23].

Similarly, the Br 3d spectra can be deconvoluted into multiple components. For BG-1, it can be fitted with three components, whereas for BG-5 and BG-20, four distinct components are identified. The deconvoluted component with a BE of 70.2 eV undoubtedly represents bromine covalently bonded to both sp^2 and sp^3 carbon atoms [23,24]. It can be seen that as the TBATB-to-rGO ratio increases, the percentage area of this component decreases, suggesting that bromine may bond to the graphene framework through different configurations. This trend is reflected in the decline of covalently bonded bromine from 96.22 % in BG-1 to 23.94 % in BG-5 and further to 14.55 % in BG-20. This effect can be attributed to the accumulation of negative charges carried by Br^- as the TBATB concentration rises, leading to steric repulsion that hinders effective bonding with the graphene structure. Consequently, the percentage of physically adsorbed Br^- (component with BE of 68.5 eV) increases from 1.86 % in BG-1 to 27.86 % in BG-5 and further to 39 % in BG-20 [1,12,23]. Furthermore, the component at a BE of 67.4 eV is associated with $C_n \rightarrow Br_2$ surface complexes, formed via charge transfer to the Br_2 molecule acting as an electron acceptor. The component at a BE of 72.9 eV corresponds to oxybrominated derivatives, as these are the only species exhibiting binding energies > 2 eV higher than those of bromine covalently bonded to carbon [23]. Additionally, only a very small fraction of bromine existed as oxybrominated derivatives, with 1.92 % in BG-1, 2.55 % in BG-5 and 0.28 % in BG-20. Table 5.2 displays the concentrations of various functional groups derived from the deconvolution of the C 1s and Br 3d spectra for all samples.

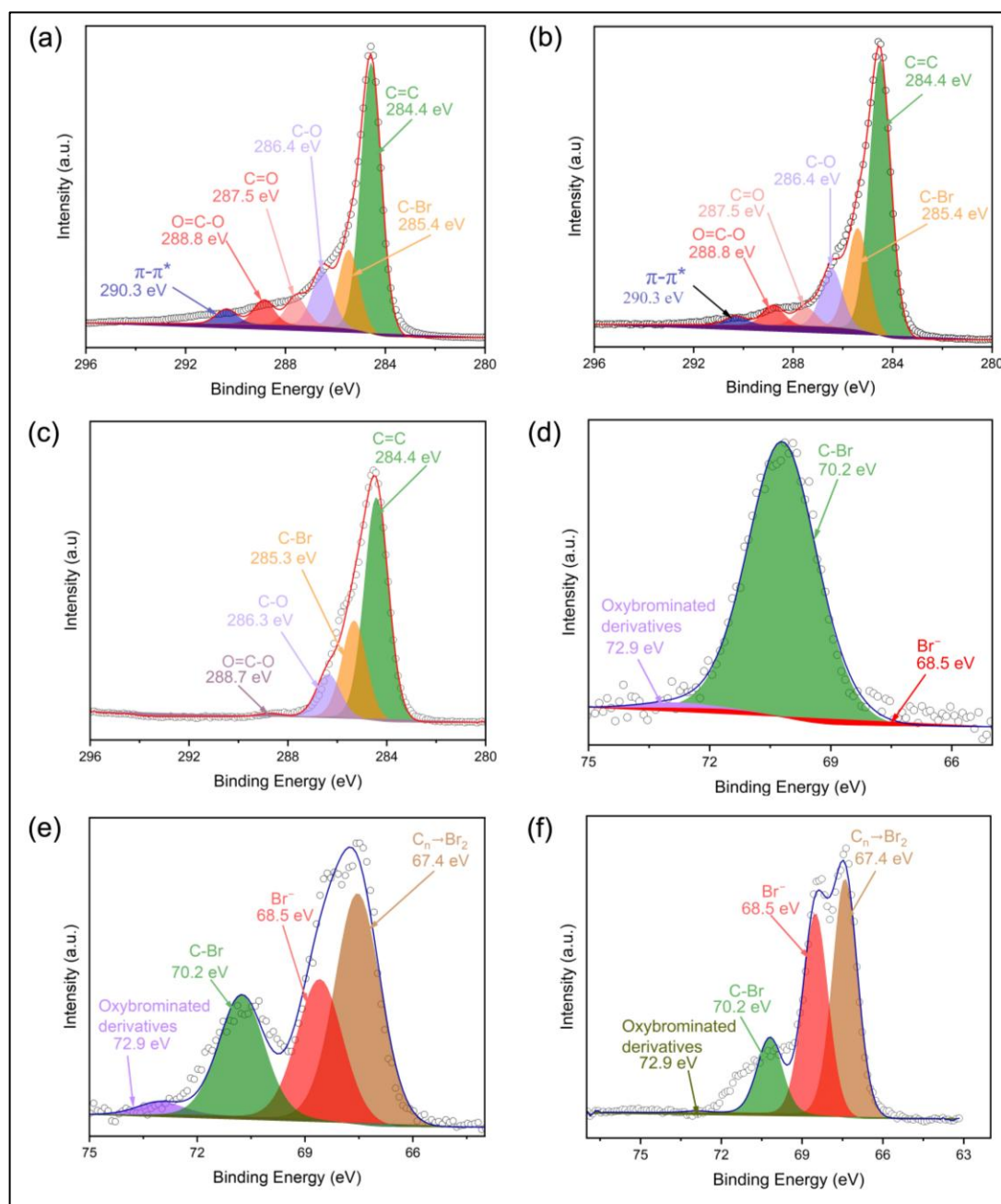


Figure 5.3. Deconvoluted HR-XPS spectra of the C 1s region of (a) BG-1 (b) BG-5 (c) BG-20. Deconvoluted HR-XPS spectra of the Br 3d region of (d) BG-1 (e) BG-5 (f) BG-20.

Table 5.2: The relative concentrations (in %) of selected functional groups, as identified from deconvoluted HR-XPS spectra of C 1s and Br 3d for all samples.

Component	C=C	C-Br	C-O	C=O	O=C-OH	$\pi-\pi^*$	$C_n \rightarrow Br_2$	Physically adsorbed Br ⁻	C-Br derivatives
Binding energy (eV)	284.4	285.4	286.4	287.5	288.8	290.3	67.4	68.5	70.2 72.9
BG-1	57.24	16.64	12	5.90	5.10	3.11	--	1.86	96.22 1.92
BG-5	57	21.02	12.19	3.88	4.07	1.84	45.65	27.86	23.94 2.55
BG-20	60.76	26.59	11.71	--	0.93	--	46.18	39	14.55 0.28

FTIR analysis was also conducted to verify the presence of C–Br bond and to identify the functional groups on the bromographene's surface. Figure 5.2 (b) displays the FTIR spectra for all samples, highlighting the existence of both C–H and C–Br bonds [11,25]. The characteristic C–Br bond appears at 572 cm^{-1} , along with several other notable absorption bands [25]. The bands observed at 1630 cm^{-1} and 1728 cm^{-1} correspond to bending mode of molecular water adsorbed on the graphene's surface and carboxylic acid groups [26–28]. The band at 1380 cm^{-1} represents sp^3 C–H bending vibrations, indicating structural defects, which are expected due to the oxidation-reduction method used for rGO synthesis [11]. Additionally, a broad peak centred at 3432 cm^{-1} is associated with the –OH stretching vibrations involved in hydrogen bonding, whereas the presence of two sharper bands around $\sim 2875\text{ cm}^{-1}$ and $\sim 2930\text{ cm}^{-1}$ confirm the formation of C–H bonds as a result of the bromination process [22,25].

Morphological and structural characterization

Field-emission scanning microscopy (FESEM) and transmission electron microscopy (TEM) were employed to investigate the surface morphology of the samples. The SEM images (Figure 5.4 (a)–(c)) show that all samples exhibit a crumpled, thin, fabric-like structure with basal planes averaging a few microns in size. These structures are closely interconnected, forming a disordered and porous network, a characteristic commonly observed in materials produced through oxidation/reduction-based methods [9,29].

Further, EDX analysis was used to assess the distribution of carbon, oxygen, bromine, and nitrogen across all samples, which showed that bromine content varied significantly with changes in the TBATB-to-rGO ratio. Specifically, BG-1 contained 0.70 wt% Br, while BG-5 and BG-20 had 8.02 wt% and 17.60 wt% Br, respectively, aligning with trend observed in the XPS measurements. Notably, the higher bromine

concentrations detected by XPS compared to SEM-EDX analysis (Table 5.3) can be attributed to the high surface sensitivity of XPS. Additionally, partial breakdown of the C–Br bond in bromographenes under UHV conditions and exposure to X-ray irradiation may also contribute to this discrepancy [11]. Given the highest bromine content, BG-20 was selected for elemental distribution mapping to elucidate the spatial distribution of constituent elements, as illustrated in Figure 5.4 (d)–(h). The mapping confirms a uniform bromine distribution throughout the BG-20 sample, suggesting that bromination occurred not only at the edges but also within the bulk of the rGO flakes [11].

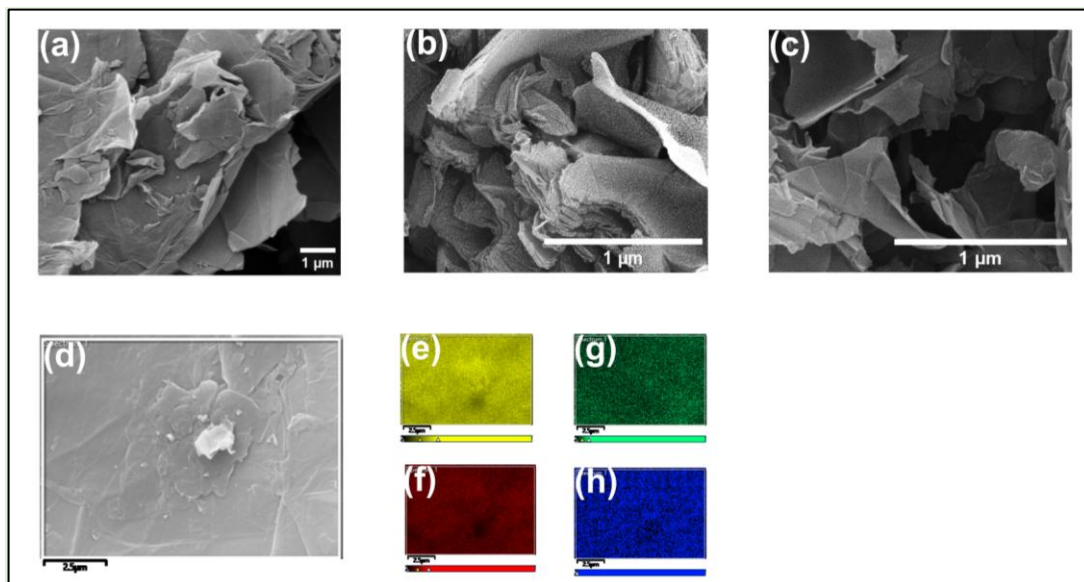


Figure 5.4. FE SEM image of (a) BG-1 (b) BG-5 (c) BG-20. (d) SEM image of BG-20 utilized for elemental mapping, with corresponding elemental distribution maps for (e) Carbon, (f) Oxygen, (g) Bromine and (h) nitrogen.

High-resolution transmission electron microscopy (HR-TEM) images of BG-1, BG-5, and BG-20, along with their corresponding selected area electron diffraction (SAED) patterns, are presented in Figures 5.5 (a)–(c). The HR-TEM micrographs reveal semi-transparent graphene sheets with a wrinkled and folded morphology, which is characteristic of chemically exfoliated and functionalized graphene materials

[19]. Most of the graphene sheets appear largely flat, while localized folding and curling are observed predominantly at the sheet edges, appearing as dark line-like features. These folded regions suggest the coexistence of few-layer and multilayer graphene domains, while the lighter, more transparent areas correspond to thinner sheets consisting of only a few graphene layers [30]. Furthermore, the HR-TEM images show uniform, continuous graphene sheets with no observable holes or discontinuities, indicating the high structural quality of the synthesized materials [19].

The insets of Figures 5.5 (a)–(c) show the SAED patterns acquired from representative regions of the samples. The SAED patterns display distinct diffraction spots arranged in a six-fold pattern, characteristic of the hexagonal graphitic lattice, confirming that the fundamental crystalline structure of graphene is preserved after bromination [30]. The primary diffraction features consist of concentric rings with interplanar spacings of approximately 0.207 nm and 0.120 nm, which can be indexed to the {100} and {110} planes of graphene, respectively [31]. The presence of ring-like diffraction patterns rather than isolated sharp spots indicates that the samples are composed of numerous randomly oriented graphene domains, reflecting their polycrystalline nature and are analogous to diffraction features observed in powder X-ray diffraction patterns [30,31].

Table 5.3: Elemental composition of bromographenes determined using SEM-EDX analysis.

Sample	wt % C	wt % N	wt % O	wt % Br
BG-1	79.93	1.21	18.15	0.70
BG-5	79.85	1.62	10.51	8.02
BG-20	73.34	3.57	5.49	17.60

X-ray diffraction (XRD) measurements were carried out to investigate the crystalline structure, stacking order, and microstructural parameters of bromographene samples.

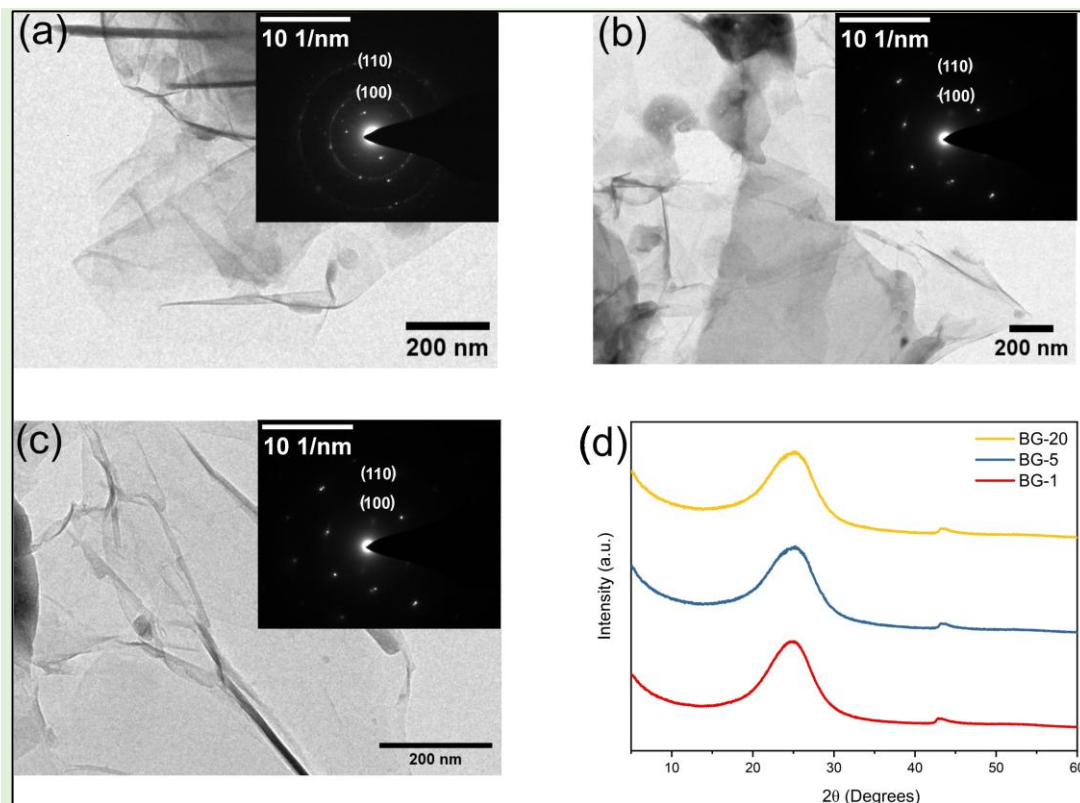


Figure 5.5. HRTEM images of (a) BG-1, (b) BG-5, and (c) BG-20; the insets show the corresponding SAED patterns. (d) XRD spectra of BG-1, BG-5 and BG-20.

Figure 5.5 (d) shows the XRD patterns of all bromographene samples. All samples exhibited (002) diffraction peak at $\sim 2\theta = 24.4^\circ$ representing the interlayer spacing of graphene, and (100) diffraction peak centred at $\sim 2\theta = 43.2^\circ$ signifying the presence of short-range order in the stacked graphene layers [32].

The interlayer spacing (d), calculated from the (002) reflection using Bragg's law, was determined to be 0.36 nm, which lies within the range typically reported for reduced graphene oxide [17]. Further, the average stacking height (L_c), representing the thickness of stacked graphene layers along the c -axis, was estimated from the full

width at half maximum (FWHM) of the (002) reflection using the Scherrer equation (Equation 5.4) [33] :

$$L_C = \frac{0.89 \times \lambda}{\beta_{002} \cos \theta} \quad (5.4)$$

where λ is the X-ray wavelength (Cu K α , 1.5406 Å), β_{002} is the FWHM of the (002) peak, and θ is the Bragg's angle. The extracted parameters are summarized in Table 5.4, and the nanometer-scale L_C values, ranging from 0.9–1.21 nm indicate short-range stacking with a limited number of graphene layers. Additionally, the in-plane crystallite size (L_a), which reflects the lateral dimension of ordered sp² domains within the graphene sheets, was estimated from the (100) diffraction peak using Equation 5.5 [19].

$$L_a = \frac{1.84 \times \lambda}{\beta_{100} \cos \theta} \quad (5.5)$$

Where, β_{100} corresponds to the FWHM of the (100) reflection. The obtained values are 9.03, 11.70 and 10.66 nm for BG-1, BG-5 and BG-20 respectively, which is consistent with the lateral area obtained from Raman analysis. Raman spectra of all bromographene samples were analyzed elaborately, in order to obtain further macroscopic information on the structure. The Raman spectra of BG-1, BG-5 and BG-20 is shown in Figure 5.6 (a), wherein the samples exhibit four characteristic features at ~1350 cm⁻¹ (D-band), ~1590 cm⁻¹ (G-band), ~2700 cm⁻¹ (2D band) and ~2940 cm⁻¹ (D+G band) [19].

Table 5.4: Comparison of structural parameters of BG-1, BG-5 and BG-20 derived from XRD analysis.

Sample	Peak (002)				Peak (100)		
	2 θ (deg)	FWHM (deg)	d (nm)	L_C	2 θ (deg)	FWHM (deg)	L_a
BG-1	24.48	6.67	0.36	1.20	43.47	1.94	9.03

BG-5	24.42	6.63	0.36	1.21	43.31	1.49	11.70
BG-20	24.77	8.86	0.36	0.91	43.33	1.64	10.66

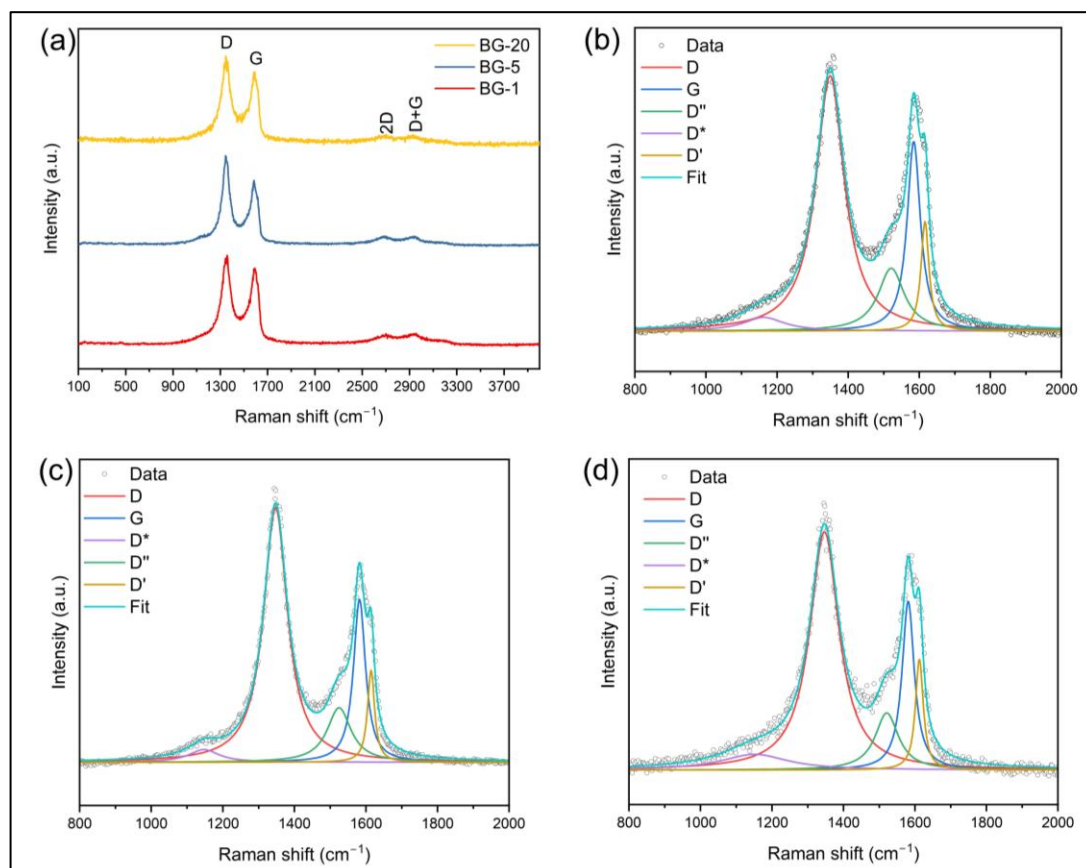


Figure 5.6. (a) Raman spectrum of BG-1, BG-5 and BG-20. Fitted Raman spectra of (b) BG-1, (c) BG-5, and (d) BG-20.

The G band arises from the in-plane vibration of sp^2 -hybridized carbon atoms (E_{2g} phonon mode) and the D band is associated with the breathing mode of six-membered sp^2 carbon rings and becomes Raman-active in the presence of defects or disruptions in the sp^2 lattice [34]. In case of chemically exfoliated graphene as in this case, the D band is attributed primarily to the sp^3 hybridized carbon atoms which may arise due to the presence of different functional groups (for instance, covalent C–Br bonding), which locally converts sp^2 -hybridized carbon into sp^3 configurations [9]. This

chemical functionalization breaks the translational symmetry of the graphene lattice, thereby activating the D band. Further, in addition to the D and G bands, the spectrum shows broad second-order features in the high-wavenumber region, typically observed at $\sim 2700\text{ cm}^{-1}$ and $\sim 2940\text{ cm}^{-1}$. The band centered near $\sim 2700\text{ cm}^{-1}$ corresponds to the 2D (also referred to as G') band, which arises from a second-order two-phonon double-resonance process and does not require defects to be Raman-active. In pristine monolayer graphene, this band is sharp and symmetric; however, in chemically exfoliated and functionalized graphene such as bromographene, the 2D band becomes broadened, weakened, and asymmetric which may be attributed to increased disorder, interlayer interactions, and disruption of the π -electron system caused by covalent functionalization [34,35]. On the other hand, the broad feature observed around and $\sim 2940\text{ cm}^{-1}$ can be assigned to combination modes, primarily the D + G band, which originates due to the combination of two phonons with different momentum and requires a defect for its activation [36,37]. Further, the ratio of the intensity of the D band and G band (represented as I_D/I_G) gives an indication of the density of the defects and degree of graphitization present in the material, where higher values reflect more defects [9]. Thus, in order to determine the I_D/I_G ratio, the D and G bands are deconvoluted into various components as shown in Figures 5.6 (b) – (d). In case of chemically exfoliated graphene-based materials, the superposition of bands can lead to ambiguity and thus, it is important to deconvolute the various bands [38]. Lee and colleagues did extensive study and found that five Lorentzian line shapes are suitable for fitting of Raman spectra and the deconvolution gives rise to the following first-order Raman modes, namely, D*, D, D'', G and D' bands [38]. The D and G bands are discussed in the earlier section and D* band which is located at $1050\text{--}1200\text{ cm}^{-1}$ is attributed to the disordered graphitic lattices [35]. The D'' band which is located at $1500\text{--}1550\text{ cm}^{-1}$ is related to the amorphous phase and its intensity is inversely related to the crystallinity. On the other hand, D' band at 1620 cm^{-1} is attributed to the intra-

valley resonance with the G band and undergoes splitting due to impurities [38]. The calculated values of I_D/I_G ratios were found to be 1.35, 1.56 and 1.41 for BG-1, BG-5 and BG-20 respectively (Table 5.5). The increase in the I_D/I_G ratio from BG-1 to BG-5 suggests an enhancement in disorder, which can be attributed to the increased introduction of defects and functional groups within the sp^2 carbon framework. The subsequent decrease in the ratio observed for BG-20 indicates partial saturation of defect sites and/or healing process and structural rearrangement of the graphene backbone takes place during higher treatment levels [38]. Further, the intensities of the bands are also useful for calculating the defect-free domains within graphene represented by the value of average crystallite size ($L_{a'}$) according to Equation 5.6 [39]:

$$L_{a'} = 2.4 \times 10^{-10} \lambda_{laser}^4 (I_G/I_D) \quad (5.6)$$

Where, λ_{laser} represents the laser excitation wavelength. Using a 532 nm laser, the calculated $L_{a'}$ values were approximately 14.2 nm for BG-1, 12.3 nm for BG-5, and 13.6 nm for BG-20. The reduced $L_{a'}$ value observed for BG-5 indicates a higher degree of disorder and defect density, followed by BG-20. The obtained $L_{a'}$ also corroborates the lateral size of the aromatic areas, as obtained from XRD.

Table 5.5: I_D , I_G , I_D/I_G and average crystallite size calculated using Raman spectroscopy.

Sample	I_D	I_G	I_D/I_G	$L_{a'}$
BG-1	1262.53	937.76	1.35	14.24
BG-5	1177.88	754.40	1.56	12.32
BG-20	344.48	244.40	1.41	13.63

Electrochemical performance

To evaluate the practical applicability of bromographene and to elucidate how the incorporation of bromo functional groups influences the charge-storage behavior of reduced graphene oxide (rGO), symmetrical coin-cell supercapacitors (Figure 5.7 (a)) were fabricated and tested. For comparison, a symmetric device based on the non-brominated rGO counterpart was also assembled following the same protocol. Electrode preparation was carried out as described in Section 2.6, with a mass loading of $\sim 1 \text{ mg cm}^{-2}$ per electrode. Prior to device assembly, the glass fibre filter paper was soaked overnight in 1-ethyl-3-methylimidazolium tetrafluoroborate to ensure complete wetting. The coin cells were then assembled as shown in Figure 5.7 (a) and the devices were crimped under a pressure of ~ 1000 psi to ensure proper sealing and mechanical stability. For ease of reference throughout this work, the symmetric supercapacitors are denoted as rGO SC, BG-1 SC, BG-5 SC and BG-20 SC, corresponding to devices fabricated using the rGO, BG-1, BG-5, and BG-20 electrode materials, respectively, as defined earlier.

The safe working potential of the devices was first evaluated by recording CV and GCD curves of the BG-20 SC at different voltage windows. As shown in Figures 5.7 (b)–(c), a pronounced rise in current response and noticeable distortion in the charge–discharge profiles appear once the applied potential exceeds a certain limit. Such behaviour, commonly, signifies the onset of electrolyte decomposition and other parasitic faradaic reactions. Based on this observation, the operating window was restricted to 0–3.0 V, and all subsequent electrochemical measurements were conducted within this range.

The CV profiles recorded for all fabricated devices at 20 mV s^{-1} is shown in Figure 5.8 (a). The CV curves were quasi-rectangular and an analysis of the curves reveals that the non-brominated counterpart i.e., rGO SC possesses the lowest enclosed area and

the area increases with the increase in bromine content, revealing that the performance follows the order: BG-20 SC > BG-5 SC > BG-1 SC > rGO SC.

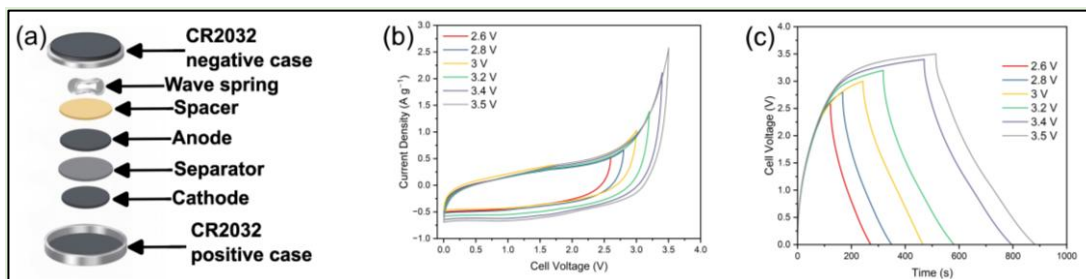


Figure 5.7. (a) Schematic illustration of the CR2032-type coin-cell assembly. (b) Cyclic voltammetry (CV) curves of the BG-20 SC recorded at a scan rate of 5 mV s^{−1} over different operating voltage windows (2.6 V–3.5 V). (c) Galvanostatic charge–discharge (GCD) profiles of BG-20 SC measured at 1 A g^{−1} under varying cell voltages (2.6 V–3.5 V).

Minor redox features are also observed for all samples, which may arise from oxygen, nitrogen, and bromine-containing functional groups remaining on the graphene framework. Further, Figure 5.8 (b) represents the CV curve for BG-20 SSC at different scan rates. Notably, the CV curves maintain an almost rectangular shape despite a high scan rate of 100 mV s^{−1}, indicating that the system predominantly exhibits capacitive behaviour. This suggests that charge transport is highly efficient both within the material and across the electrode-electrolyte interfaces [19]. Since, the overall charge-storage behaviour can be attributed to the combined contributions of electric double-layer capacitance and diffusion-controlled pseudocapacitive processes. Thus, to further elucidate the charge-storage kinetics and to quantify the capacitive and diffusion-controlled contributions, both the power law analysis and Dunn's method were employed. According to the power law approach, the relationship between the peak current (i) and the scan rate (v) is expressed as:

$$i = av^b \quad (5.7)$$

Or,

$$\log i = \log a + b \log v \quad (5.8)$$

Where, a and b are adjustable parameters in the equation and the b -value indicates the dominant charge-storage mechanism. A b -value of 0.5 indicates that the current response is proportional to the square root of the scan rate ($i \propto v^{1/2}$), which is characteristic of diffusion-controlled processes. In contrast, a b -value of 1 signifies that the current response varies linearly with the scan rate ($i \propto v$), reflecting a predominantly surface-controlled capacitive behaviour. Intermediate b -values between 0.5 and 1 therefore imply mixed charge-storage contributions arising from both capacitive and diffusion-limited processes. By plotting $\log i$ vs. $\log v$ (inset of Figures 5.8 (d) – (f)) for the anodic and cathodic peaks, the b -values for all devices were obtained and is presented in Figures 5.8 (d) – (f).

In our case, the rGO SC exhibits $b \approx 0.50$, implying that its charge storage is largely limited by ion diffusion. In contrast, the bromographene series shows systematically higher b -values, namely BG-1: ~ 0.60 , BG-5: ~ 0.70 , and BG-20: ~ 0.70 , evidencing a clear shift toward more surface-controlled kinetics after bromination. This trend is consistent with the broader literature on functionalized graphene, where conversion of local sp^2 domains into sp^3 domains, defect creation, and surface-chemistry modification can (i) increase electrochemically accessible sites, (ii) improve electrolyte wetting/ion access, and (iii) suppress restacking which collectively enhances the performance [17,40]. Additionally, the charge-storage mechanisms were quantitatively analysed by deconvoluting the total current response into capacitive and diffusion-controlled contributions at different scan rates using Dunn's method. According to this approach, the current response in a CV profile at any given scan rate and at any potential can be described as the sum of capacitive and diffusion-controlled

components ($i = i_{capacitive} + i_{diffusion}$). At a fixed voltage, the current density ($i(V)$) on a CV curve is expressed as:

$$i(V) = k_1 v + k_2 v^{1/2} \quad (5.9)$$

Where, k_1 and k_2 represents the capacitive and diffusion-controlled process and $k_1 v$ and $k_2 v^{1/2}$ correspond to capacitive and diffusion-controlled contributions respectively. Equation 5.9 can be rewritten as:

$$i(V)/v^{1/2} = k_1 v^{1/2} + k_2 \quad (5.10)$$

Accordingly, the values of $i(V)$ obtained from CV curves recorded at various scan rates were used to construct plots of $i(V)/v^{1/2}$ vs. $v^{1/2}$, where the slope corresponds to k_1 and the y-intercept corresponds to k_2 . Substituting the extracted k_1 and k_2 value into Equation 5.9 enables isolation of the capacitive and diffusive contribution at each potential. The percentage contributions of capacitive and diffusion-controlled currents at different scan rates were quantified and are presented as bar diagrams in Figures 5.9 (a)–(d).

Generally, diffusion-controlled processes dominate at lower scan rates, as there is sufficient time for electrolyte ions to penetrate the bulk and interior pores of the electrode. Conversely, as the scan rate increases, the reduced timescale restricts deep ion diffusion, favouring surface-controlled capacitive charge storage. Accordingly, rGO SC exhibits a predominantly diffusion-controlled mechanism, showing a capacitive contribution of only 6.3 % at 5 mV s^{-1} , which increases moderately to 23.12 % at 100 mV s^{-1} . In contrast, the bromographene devices demonstrate significantly higher capacitive contributions. At a high scan rate of 100 mV s^{-1} , the capacitive contributions are 70.49 % (BG-1 SC), 38.68 % (BG-5 SC), and 49.49 % (BG-20 SC) and these values decrease to 34.82 %, 12.36 % and 17.94 % at 5 mV s^{-1} respectively.

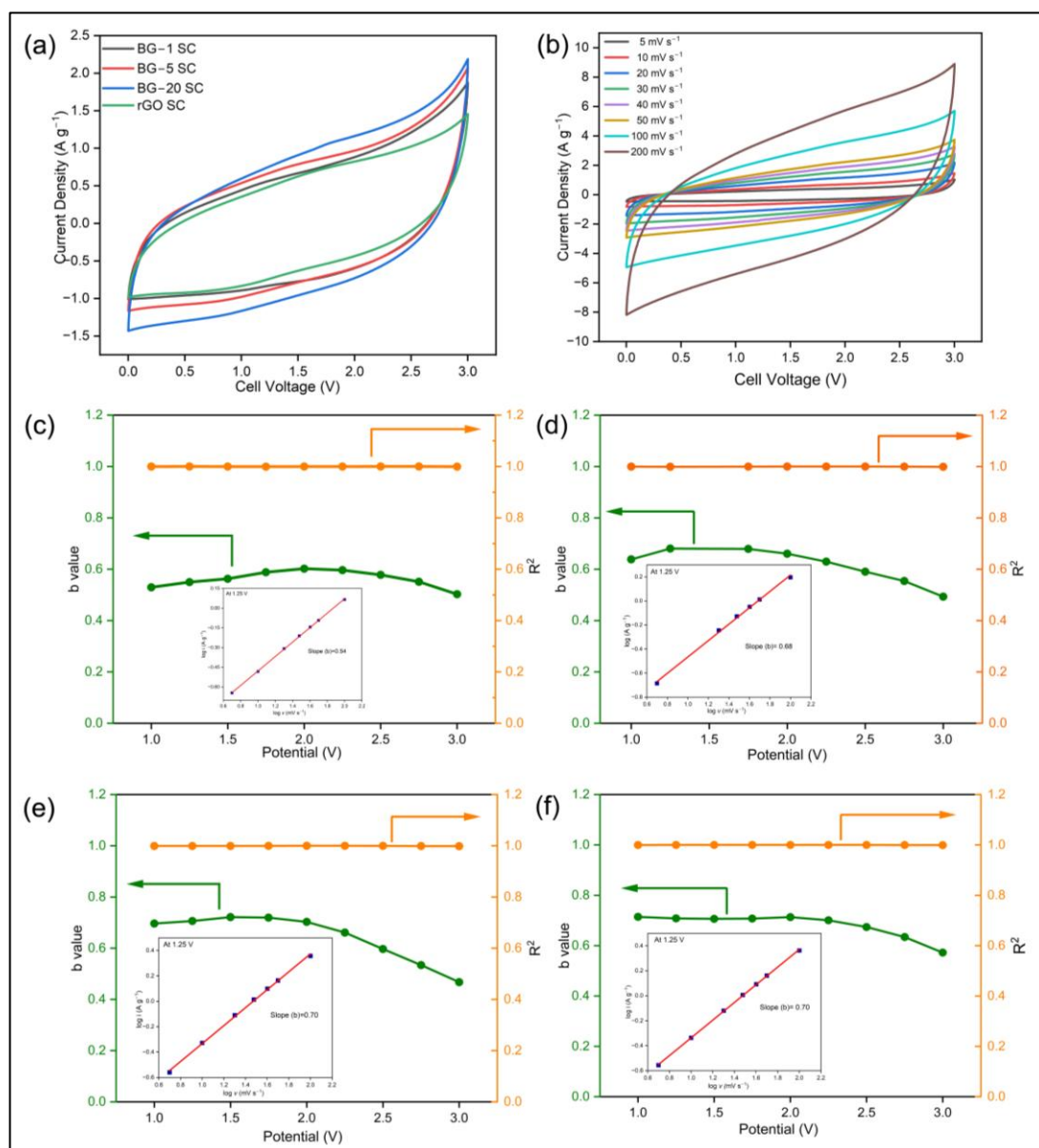


Figure 5.8. (a) CV responses of rGO SC, BG-1 SC, BG-5 SC and BG-20 SC at scan rate of 20 mV s^{-1} within the optimized voltage window of 3 V. (b) CV responses of BG-20 SC at various scan rates. Variation of the b-value with applied potential for the devices (c) rGO SC, (d) BG-1 SC, (e) BG-5 SC and (f) BG-20 SC obtained from fitting of current versus scan rate ($i = av^b$). The inset displays a representative $\log(i)$ versus $\log(v)$ plot, while the corresponding R^2 values confirm the reliability of the fitting.

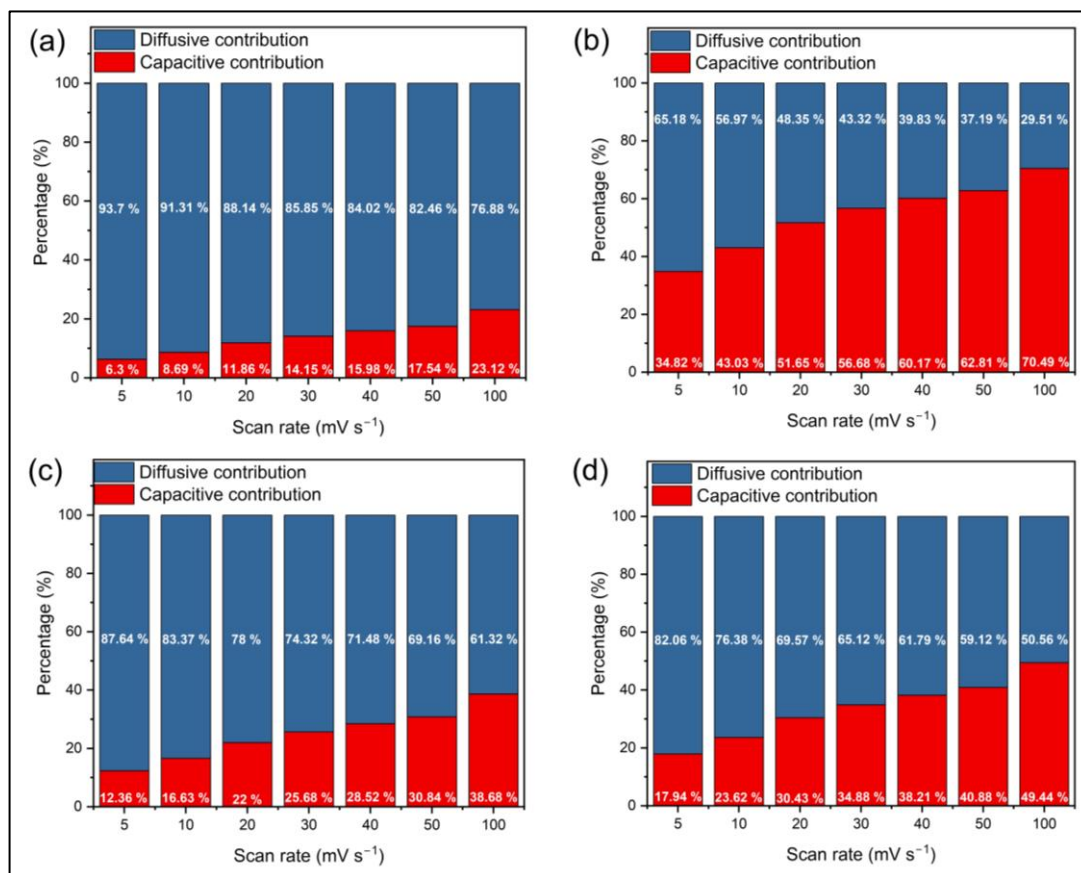


Figure 5.9. Capacitive–diffusive contribution analysis of the symmetric supercapacitor devices. Relative capacitive and diffusion-controlled charge storage contributions at different scan rates for (a) rGO SC, (b) BG-1 SC, (c) BG-5 SC and (d) BG-20 SC.

Figures 5.10 (a)–(d) presents the capacitive–diffusive current deconvolution plots for all devices at a scan rate of 20 mV s⁻¹. The light blue colour shaded regions correspond to the surface-controlled (capacitive) contribution extracted using Dunn’s method. The rGO–SC device exhibits the smallest capacitive fraction, and upon bromine functionalization, the capacitive region expands across the potential window, indicating an enhanced contribution from fast surface-controlled charge-storage processes.

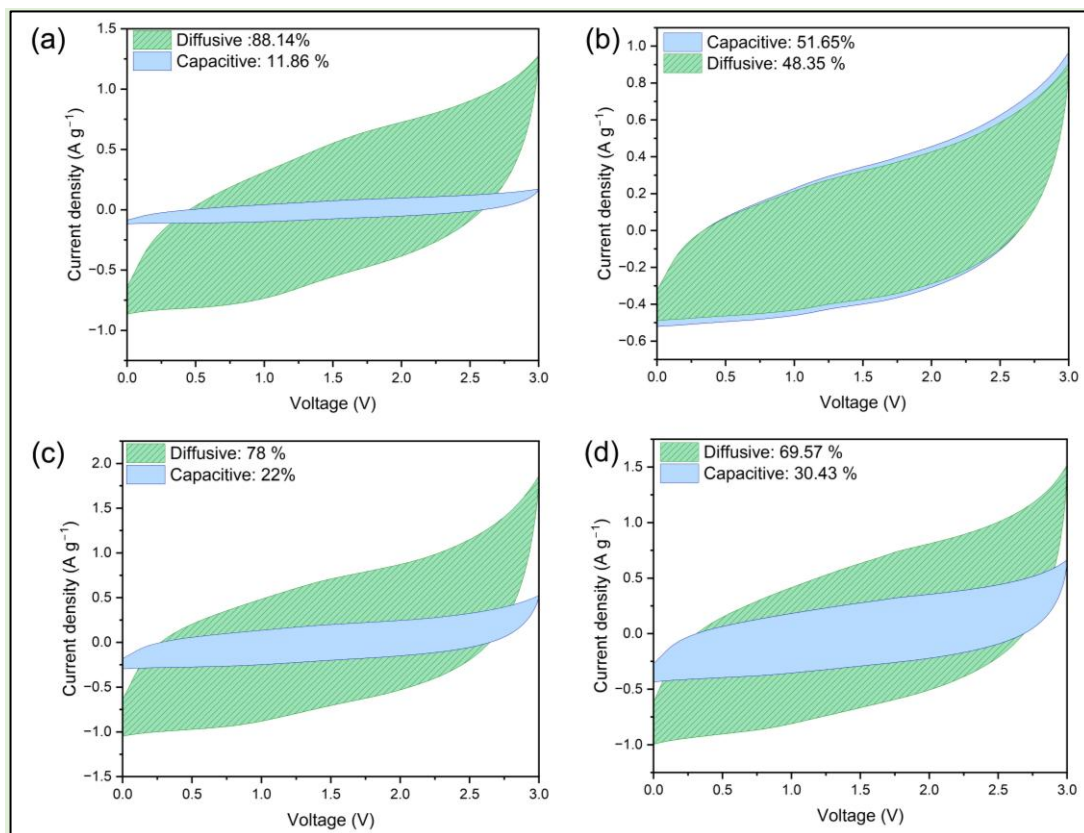


Figure 5.10. Differentiation of charge storage contributions from the CV curves of (a) rGO SC, (b) BG-1 SC, (c) BG-5 SC and (d) BG-20 SC, at a scan rate of 20 mV s^{-1} . The total current response is deconvoluted into capacitive (light blue shaded region) and diffusion-controlled (olive green shaded region) components.

This enhanced capacitive behaviour in the bromographene samples aligns with the b-value analysis, confirming a progressive shift from diffusion-controlled to surface-controlled charge-storage mechanisms following functionalization. These modifications promote surface-controlled capacitive charge storage in addition to diffusion-controlled processes. Consequently, the bromographene devices exhibit higher capacitive fractions and improved electrochemical performance.

These findings were further validated through GCD measurements. Figure 5.11 (a) presents the GCD profiles of rGO SC, BG-1 SC, BG-5 SC, and BG-20 SC recorded at a current density of 2 A g^{-1} . Notably, the BG-20 SSC exhibits a significantly longer

discharge time compared to BG-5 SC, BG-1 SC and rGO SC, indicating a higher specific capacitance.

Table 5.6: Comparison of energy and power densities of graphene-based materials as supercapacitor electrodes.

System	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)	Ref.
CoNi ₂ S ₄ @rGO // Fe ₂ O ₃ @rGO	37.83	750	[41]
Graphene@NiO nanosheets	43.2	500	[42]
RGO@ZnO–SnO ₂ // AC	26	750	[43]
MnFe ₂ O ₄ /rGO // AC	28.12	750	[44]
NiO/MnO ₂ /GO // MWCNT	28	750	[44]
Ni ₃ Si ₂ /NiOOH/graphene	25.9	750	[45]
Zn–Co–Mo–rGO // AC	14	750	[46]
NiCo ₂ S ₄ /rGO // AC	24.4	750	[47]
h-BN/rGO/CdS@PPy // AC	32	750	[48]
Gr/BiOBr	29.2	700	[49]
PYT/GN 4–5//A–Ti ₃ C ₂ T _x	18.4	700	[50]
CeO ₂ @γ-Fe ₂ O ₃ // rGO	36.8	700	[51]
rGO/PPy	21.4	453	[52]
rGO/GQDs	22.2	500	[53]
N/S co-doped GNRs	23.85	488	[54]
Ru/MnO _x /rGO	22.26	166	[55]
BG-20 SC	46.44	750	This work
BG-5 SC	39.46	750	
BG-1 SC	29.77	750	
rGO SC	25.12	750	

A clear progressive enhancement in capacitive performance is observed following the sequence rGO SC < BG-1 SC < BG-5 SC < BG-20 SC, demonstrating that increasing bromine content directly correlates with improved electrochemical performance. The specific capacitance (C_{SP}) values were calculated from the GCD curves using Equation 5.1. At a current density of 1 A g^{-1} , BG-20 SC delivers a high C_{SP} of 148.6 F g^{-1} , followed by BG-5 SC (126.27 F g^{-1}), BG-1 SC (95.27 F g^{-1}), and rGO SC (44.93 F g^{-1}). Relative to the non-brominated rGO SC, these values correspond to performance enhancements of 112 % for BG-1 SC, 181 % for BG-5 SC, and an exceptional 230 % for BG-20 SC. These results clearly confirm that the introduction of bromine functional groups leads to a substantial improvement in charge-storage capability and overall device performance. Figure 5.11 (b) displays the GCD curves of BG-20 SC measured at various current densities ranging from 1 to 10 A g^{-1} . The curves exhibit a nearly symmetric triangular shape with slight curvature, suggesting good capacitive behaviour, high coulombic efficiency, and excellent electrochemical reversibility. Furthermore, Figure 5.11 (c) illustrates the specific capacitance of all devices across current densities from 1 to 10 A g^{-1} which follows the same trend wherein BG-20 SC delivers the best performance. In addition to enhanced capacitance, the brominated graphene devices demonstrate outstanding energy and power density characteristics. Compared to rGO SC, which delivers an E_d of $25.125 \text{ Wh kg}^{-1}$ at a P_d of 750 W kg^{-1} , BG-20 SC exhibits a remarkable 84.8 % enhancement, achieving an E_d of 46.44 Wh kg^{-1} at the same power density. Similarly, BG-5 SC and BG-1 SC show energy density improvements of 57.1 % (39.49 Wh kg^{-1}) and 18.5 % (29.77 Wh kg^{-1}), respectively. Figure 5.11 (d) presents the variation of energy density with power density for all the devices. Notably, BG-20 SC delivers energy densities of 46.44 Wh kg^{-1} at 750 W kg^{-1} , 31.79 Wh kg^{-1} at 1500 W kg^{-1} , and 26.75 Wh kg^{-1} at 2250 W kg^{-1} .

To benchmark the electrochemical performance against previously reported systems, they are shown in Figure 5.11 (e) as a Ragone plot (Table 5.6).

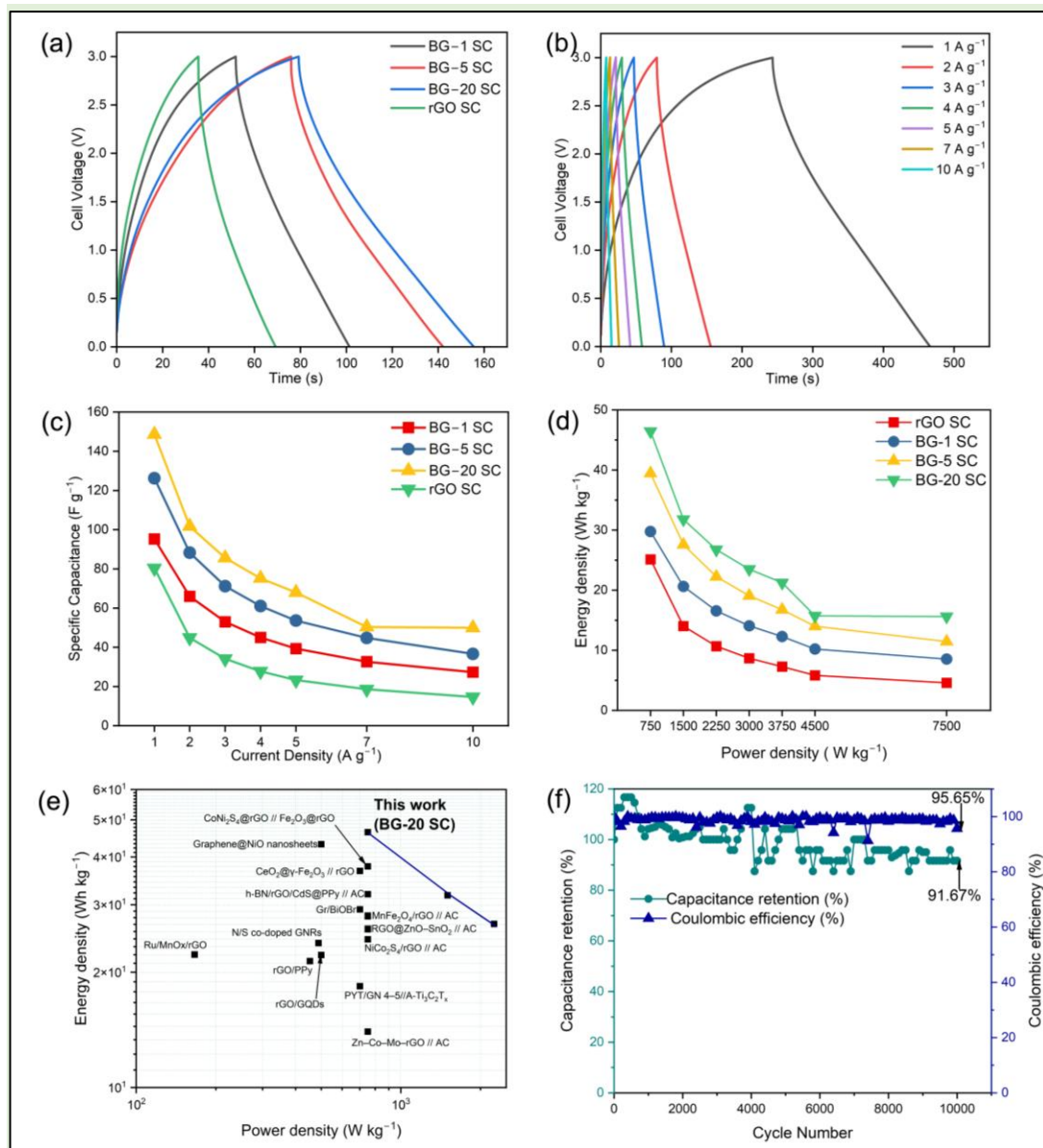


Figure 5.11. Electrochemical performance of the supercapacitor devices. (a) GCD curves of rGO-SC, BG-1 SC, BG-5 SC and BG-20 SC recorded at a current density of 2 A g⁻¹. (b) GCD curves of BG-20 SC at varying current densities (1–10 A g⁻¹). (c) Variation of specific capacitance of rGO-SC, BG-1 SC, BG-5 SC and BG-20 SC at different current densities (1–10 A g⁻¹). (d) Energy density as a function of power density for rGO-SC, BG-1 SC, BG-5 SC and BG-20 SC. (e) Ragone plot. (f) Cyclic stability of BG-20 SSC evaluated at 20 A g⁻¹ for 10,000 cycles.

This plot helps visualize the correlation between energy density and power density, demonstrating the strong performance of BG-20 SC. Thus, the energy and power densities are comparable to, and in several cases exceed, those of state-of-the-art rGO-based electrodes and their composites. Furthermore, cycling stability, which is essential for the long-term reliability of supercapacitor devices, was investigated for BG-20 SC. The device exhibits outstanding durability, retaining 91.67 % of its initial specific capacitance after 10,000 charge–discharge cycles at 20 A g^{-1} (Figure 5.11 (f)), thereby confirming its superior long-term performance. Additionally, to demonstrate the practical applicability of the fabricated supercapacitor device, two BG-20 SC were connected in series and used to power a red light-emitting diode (LED). The LED has a forward operating voltage of 1.65–2.0 V and a rated forward current of 20 mA. After charging the series-connected supercapacitors to the required voltage, the stored energy was sufficient to continuously illuminate the LED for more than 33 minutes under ambient conditions (Figures 5.12 (a)–(e)). This result confirms the ability of the assembled supercapacitor device to deliver stable power over an extended duration, highlighting its potential for energy-storage applications.

Electrochemical impedance spectroscopy (EIS) was also carried out to gain deeper insight into the charge transport processes, electrode–electrolyte interfacial behaviour, and frequency-dependent electrochemical response of the bromographene electrode. EIS is an effective technique for examining the resistive and capacitive characteristics of electrochemical systems through the application of a small AC perturbation across a broad frequency range. The impedance response is typically presented as Nyquist and Bode plots and interpreted using equivalent circuit models, in which each circuit element represents a specific physicochemical process, enabling detailed analysis of ohmic losses, charge-transfer resistance, and mass-transport phenomena in supercapacitor systems. Figure 5.12 (f) presents the Nyquist plots for all the tested supercapacitors, while Figure 5.12 (g) shows the corresponding Bode plots. The

determination of various electrochemical parameters was carried out by analysing the EIS data and fitting them using different equivalent circuit models. Both representations were employed to ensure reliable fitting, and the most suitable model was selected based on the lowest χ^2 value (Table 5.7). After several fitting attempts, the equivalent circuit that exhibited the best agreement with the experimental data is shown as an inset in Figure 5.12 (h), with the extracted circuit parameters and fitting errors summarized in Table 5.7. The Nyquist plots display a depressed semicircle in the high-frequency region, a feature typically reported for supercapacitor electrodes and associated with interfacial and charge-transfer processes. At high frequencies, the ions of ionic liquid electrolyte EMIMBF₄ (EMIM⁺ and BF₄⁻) do not have sufficient time to respond to the applied AC perturbation and, therefore, cannot fully form the electrical double layer at the electrode surface. As a result, the Nyquist plot exhibits a high-frequency intercept on the x-axis corresponding to solution resistance (R_s) represented by a series resistor (R_s) with values of 1.49 Ω , 1.18 Ω , 1.16 Ω and 1.21 Ω for rGO SC, BG-1 SC, BG-5 SC and BG-20 SC respectively (Table 5.7). The slightly lower resistance observed for the bromographene-based electrodes suggests improved electrode–electrolyte contact and ion accessibility compared to rGO. As the frequency decreases to the high-to-mid frequency range, the EMIM⁺ and BF₄⁻ ions begin to partially respond to the applied AC perturbation, leading to the onset of electrical double-layer formation at the electrode–electrolyte interface. This results in the appearance of a depressed semicircle, commonly observed in carbon-based supercapacitor electrodes, which is associated with interfacial polarization (charge transfer) resistance. In the equivalent-circuit fitting, this contribution is modelled as R_{CT} (Table 5.7) and the extracted values are 13.31 Ω , 10.07 Ω , 12.50 Ω and 4.87 Ω for rGO SC, BG-1 SC, BG-5 SC and BG-20 SC respectively. Notably, BG-20 SC exhibits a significantly lower charge transfer resistance compared to the other electrodes, reflecting enhanced electrode–electrolyte interactions and more efficient ion transport at the interface. This reduced resistance is consistent with the superior

electrochemical performance of BG-20 SC observed in the CV and GCD measurements, and supports its improved charge-transfer kinetics relative to rGO SC, BG-1 SC, and BG-5 SC.

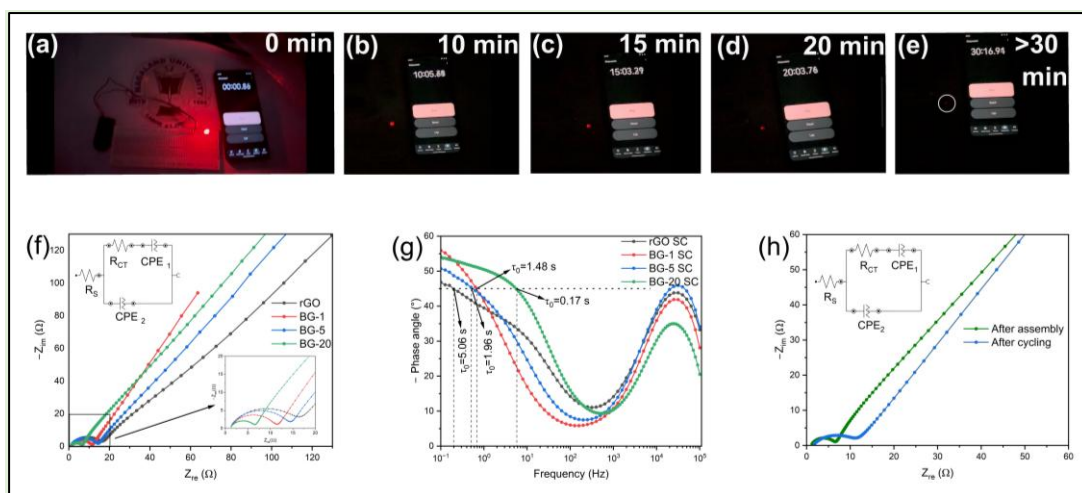


Figure 5.12. Photographs demonstrating two BG-20 SC devices connected in series to power a red LED at (a) 0 min (b) 10 min (c) 15 min (d) 20 min and (e) > 30 mins. (f) Nyquist plots of rGO-SC, BG-1 SC, BG-5 SC and BG-20 SC (inset displays the circuits used for fitting the EIS curves). (g) Bode plot of rGO-SC, BG-1 SC, BG-5 SC and BG-20 SC along with their corresponding relaxation times. (h) Nyquist plots of BG-20 SC before and after cycling (inset displays the circuits used for fitting the EIS curves).

Further, constant phase elements (CPEs) were introduced in the equivalent circuit to account for the non-ideal capacitive behaviour of the devices. CPE_1 connected in series with R_{CT} , represents the non-ideal interfacial capacitive response associated with electrical double-layer formation at the electrode–electrolyte interface. The corresponding n values lower than unity indicate significant deviation from ideal capacitive behaviour, which can be attributed to surface heterogeneity, and porous morphology of the electrodes. On the other hand, CPE_2 is connected in parallel with the R_{CT} – CPE_1 branch, dominates the low-frequency impedance response and

corresponds to capacitive charge storage associated with ion penetration and redistribution within the porous electrodes. The n values of CPE_2 are closer to unity, indicating pronounced capacitive behaviour at longer time scales and effective ionic transport both within the bulk material and at the interfaces [19,20].

Table 5.7: Circuit element values and fitting errors for the equivalent circuit model (inset of Figure 5.12 (f) and (h)) obtained from EIS data at OCP.

Device	Circuit Element		Value	Estimated Error (%)	χ^2
rGO SC	R_s		1.4863	3.606	0.040
	R_{CT}		13.312	1.499	
	CPE_1	Y_0	7.8037×10^{-6}	11.930	
		n	0.8554	1.246	
	CPE_2	Y_0	0.0050437	0.864	
		n	0.53344	0.644	
BG-1 SC	R_s		1.1832	2.872	0.030
	R_{CT}		10.067	0.853	
	CPE_1	Y_0	1.3877×10^{-5}	8.993	
		n	0.8348	0.981	
	CPE_2	Y_0	0.012796	0.827	
		n	0.67357	0.578	
BG-5 SC	R_s		1.1651	3.513	0.038
	R_{CT}		12.501	1.043	
	CPE_1	Y_0	9.0074×10^{-5}	9.859	
		n	0.8557	1.035	
	CPE_2	Y_0	0.0075949	0.884	
		n	0.60931	0.623	

BG-20 SC (Before cycling)	R_s		1.2079	2.520	0.160
	R_{CT}		4.8744	1.468	
	CPE_1	Y_0	9.094×10^{-6}	14.37	
		n	0.90769	1.429	
	CPE_2	Y_0	0.0061377	0.816	
		n	0.63305	0.443	
BG-20 SC (After cycling for 10,000 cycles @ 20 A g ⁻¹)	R_s		1.4644	1.256	0.081
	R_{CT}		10.447	1.018	
	CPE_1	Y_0	0.000332	7.118	
		n	0.62817	1.063	
	CPE_2	Y_0	0.016564	1.409	
		n	0.63722	0.945	

Bode plots were further analyzed to gain insight into the frequency-dependent electrochemical response of the supercapacitor electrodes (Figure 5.12 (g)). The frequency at which the phase angle reaches -45° , referred to as the knee frequency (f_0), represents the transition point where resistive and capacitive contributions are equal and is commonly used to estimate the relaxation time ($\tau_0 = 1/f_0$) of supercapacitor systems. A shorter relaxation time indicates faster electrochemical kinetics and improved rate capability. The knee frequencies of the rGO SC, BG-1 SC, BG-5 SC, and BG-20 SC were determined to be 0.20, 0.68, 0.51 and 5.78 Hz, corresponding to relaxation times of 5.06, 1.48, 1.96 and 0.17 s, respectively. Thus, among the investigated devices, BG-20 SC exhibits the shortest relaxation time (τ_0), confirming its rapid charge–discharge response and superior performance.

Electrochemical impedance spectroscopy (EIS) was further employed to re-evaluate the BG-20 supercapacitor after 10,000 charge–discharge cycles in order to assess its

long-term electrochemical durability. Figure 5.12 (h) compares the Nyquist spectra recorded at open-circuit potential (OCP) before and after 10,000 cycles @ 20 A g^{-1} , where the pre-cycling spectra are identical to those shown in Figure 5.12 (f). The post-cycling impedance data were fitted using the same equivalent circuit model employed for the initial analysis, and the extracted circuit parameters along with the fitting errors are summarized in Table 5.7.

Overall, the circuit elements exhibit qualitatively similar behaviour before and after cycling, indicating minimal degradation of the electrode properties. The solution resistance (R_s) shows a slight increase of just over $0.26 \text{ } \Omega$, while the interfacial polarization resistance (R_{CT}) increases by approximately $5.57 \text{ } \Omega$. This modest rise in R_{CT} can be attributed to minor aging effects of the electrode active material, such as increased surface roughness and interfacial irregularities, which lead to a small enhancement of the interfacial polarization resistance at the electrode–electrolyte interface. Despite these changes, the overall impedance response remains largely unchanged, demonstrating the excellent electrochemical stability of the BG-20 electrode. These results confirm that BG-20 SC maintains enhanced electrochemical activity while exhibiting robust long-term cycling stability, underscoring its suitability as an active electrode material for supercapacitor applications.

5.2.3 Conclusion

The study presents a rapid and environmentally friendly approach for the synthesis of bromographene, addressing the challenges of conventional techniques, which often involve harsh conditions and toxic reagents. A key advancement of this approach is the use of a greener brominating agent, tetrabutylammonium tribromide (TBATB), as an alternative to hazardous reagents like bromine and hydrobromic acid. TBATB facilitates the bromination of reduced graphene oxide under milder conditions,

reducing both environmental impact and toxicity concerns associated with traditional methods.

One of the major advantages of this method is its exceptional efficiency, achieving complete bromination of rGO in just 60 minutes, a substantial improvement over existing protocols that typically require 24 hours or more. Notably, this process is the fastest reported technique for brominating graphene and achieves one of the highest bromine contents recorded in the literature, with an impressive 4.73 % bromination, as confirmed by XPS analysis. Additionally, this study is the first to demonstrate the bromination of graphene using rGO instead of the conventional graphene oxide, thereby eliminating the need for additional processing steps. A range of analytical techniques, including FTIR, XRD, FESEM, HRTEM, Raman and XPS, were utilized to characterize the synthesized bromographene. XPS and FTIR analysis confirmed the successful bromination of rGO. FESEM and HRTEM imaging revealed a wrinkled, sheet-like morphology, while elemental mapping demonstrated a uniform distribution of bromine across the graphene matrix. Beyond its efficient synthesis, the developed material exhibits outstanding electrochemical properties. A symmetric supercapacitor fabricated using bromographene delivered a remarkable specific capacitance of 148.6 F g⁻¹, representing a ~230 % improvement over rGO (44.93 F g⁻¹). Additionally, the BG-20 SSC demonstrated an energy density of 46.44 Wh kg⁻¹ at a power density of 750 W kg⁻¹, an 84.8 % enhancement compared to rGO SSC (25.125 Wh kg⁻¹). The obtained energy density is one of the highest reported for graphene-based materials and surpasses many rGO-based composites. The material also showcased excellent cyclic stability, retaining 91.67 % of its charge after 10,000 cycles, highlighting its potential for long-term applications. These findings confirm that bromine functionalization significantly enhances the electrochemical properties of rGO, providing an effective approach for the development of next-generation, high-performance energy storage systems. Furthermore, the synthesized bromographene

can also serve as a versatile platform for further chemical modifications, broadening its potential applications.

Section-II

A comparative study on the bromination of reduced graphene oxide using different tribromides

5.3. Introduction

In recent years, the chemical functionalization of graphene has emerged as a major focus within materials science research [17]. This growing interest stems from the ability to fine-tune graphene's physical and chemical properties by introducing specific types and amounts of groups onto its structure[17,56]. Incorporating heteroatoms or chemically reactive functionalities not only alters graphene's reactivity, chemistry, surface energy, but also leads to significant improvements in the performance of functionalized graphene in areas such as gas sensing [57], energy storage [58], catalysis [59], and biosensing [60]. For instance, Mazzotta and colleagues [61] reported that functionalization of graphene with dimethyl acetylenedicarboxylate led to a marked improvement in electrochemical performance. The functionalized graphene exhibited a discharge capacity of 162.3 mAh/g and reached a coulombic efficiency of 95% within a few cycles, while the unmodified sample showed only 56.3 mAh/g capacity and 8.4% efficiency. Moreover, the functionalized material retained 57% of its capacity at a high C-rate of 10C, demonstrating enhanced rate capability and stability. In another report, Beyranvand et al. [62] found that graphene functionalized with boronic acid demonstrated potent antibacterial and antiparasitic activity and significantly accelerate diabetic wound healing, achieving complete discourse of infected non infected wounds within 10 days. Besides the widely studied graphene derivatives such as graphene oxide (GO) [16], reduced graphene oxide (rGO)[63] , and fluorographene [64], halogenated forms like bromo-functionalized reduced graphene oxide, or bromographene, remain relatively unexplored and underreported in the literature [11]. This limited attention is likely due

to the reliance on toxic reagents like liquid bromine and hydrobromic acid, as well as the typically long and cumbersome processing steps involved. Despite these challenges, bromographene holds significant potential, as the carbon–bromine bonds can serve as reactive sites for further chemical modification. This versatility opens pathways to introduce a wide range of organic functional groups, broadening its utility in advanced materials and device applications. To illustrate, Rabchinskii and colleagues reported a simple two-step method for synthesizing aminated graphene. In the first step, GO was brominated using hydrobromic acid, producing brominated GO with a significant amount of covalently attached bromine. This was followed by treatment with an ammonia solution, which effectively substituted the bromine atoms with primary amine ($-NH_2$) groups, yielding aminated reduced graphene oxide. Similarly, Zou and colleagues achieved selective bromination of reduced graphene oxide using 1,3-dibromo-5,5-dimethylhydantoin (DBMH) in a mixture of trifluoromethanesulfonic acid and dichloromethane at room temperature. The resulting brominated graphene was subsequently post-functionalized with 4-pyridinyl boronic acid through Suzuki coupling, enabling the successful attachment of pyridine groups to the graphene framework.

Therefore, developing a solution-phase bromination method that operates under mild, controllable laboratory conditions using safer reagents would be a valuable advancement. Compared to existing bromination methods that rely on highly toxic reagents such as liquid bromine or hydrogen bromide, and require specialized equipment like UV lamps or plasma systems under harsh conditions, tribromides offer a safer, more practical, and environmentally friendly alternative.

Herein, we report a simple, efficient, and scalable strategy for the bromination of reduced graphene oxide (rGO) employing a range of tribromide reagents as brominating agents. The method developed in this work, though simple, is highly versatile and may be readily extended to other tribromides beyond those demonstrated.

To demonstrate the universality of the developed approach, several quaternary ammonium tribromides (QATBs) were synthesized and utilized under identical experimental conditions to achieve bromination of rGO. A comparative analysis of their reactivity and influence on the structural, morphological, and chemical features of the resulting brominated products was subsequently performed.

The present work thereby establishes a universal and adaptable bromination protocol that circumvents the use of conventional, hazardous brominating agents such as liquid bromine or N-bromosuccinimide, while maintaining high efficiency and reproducibility. Notably, the bromination process is completed within just 60 minutes, in contrast to the several hours typically required in conventional methods reported in the literature. Further, the degree of bromination and bonding nature vary significantly depending on the type of tribromide used. Such differences are critical for tailoring functionalization strategies and selecting appropriate reagents. In addition, the C–Br bonds in the resulting brominated rGO serve as versatile reactive sites that can be readily substituted with various organic groups, offering a promising route for the design of advanced graphene-based functional materials. Moreover, this methodology can also be extended for the bromination of other materials, such as activated carbon, carbon nanotubes, offering a general framework for brominating diverse nanostructures.

5.3.1 Materials and methods

Chemicals and materials

Graphite (< 20 μm), sulfuric acid (98%) and sodium hydroxide pellets were obtained from Sigma-Aldrich. Sodium carbonate (99.5%), tetrabutylammonium bromide (99%), potassium bromide (99.5%), acetonitrile (99%), sodium nitrate (99%), potassium permanganate (99%), L-Ascorbic acid (99.7%) and acetonitrile (99.5%)

were obtained from Sisco Research Laboratories Pvt. Ltd., India. Hydrogen peroxide (50%) was purchased from Thermo Fisher Scientific India Pvt. Ltd. The chemicals were used as received and deionized (DI) water (Resistivity 18.2 M Ω cm @ 25°C) was used during the experiment.

Synthesis of quaternary ammonium tribromides (QATBs)

Quaternary ammonium tribromides (QATBs) were synthesized via an oxidative bromination strategy employing vanadium pentoxide (V₂O₅) as a catalyst and hydrogen peroxide (H₂O₂) as the oxidant. A schematic representation of the synthesis is shown in Figure 5.13. In a typical procedure, V₂O₅ was added gradually to a pre-cooled beaker containing 30% H₂O₂ maintained at 0–5 °C, generating a reddish-brown peroxovanadium solution. Since the V₂O₅–H₂O₂ reaction is highly exothermic, the mixture was kept in an ice bath throughout the experiment. Subsequently, an aqueous solution of potassium bromide (KBr) and the desired quaternary ammonium bromide was introduced, followed by slow addition of 1 M H₂SO₄ under continuous stirring. The reaction mixture was maintained at 0–5 °C until yellow to orange crystalline precipitates formed, which were isolated by suction filtration, thoroughly washed with water, and dried in a vacuum desiccator over anhydrous CaCl₂.

The specific syntheses were performed as follows

Tetraethylammonium tribromide (TEATB).

V₂O₅ (0.05 g, 0.27 mmol) was added to a pre-cooled 250 mL beaker containing H₂O₂ (5 mL, 44.12 mmol). To the resulting solution, KBr (5.67 g, 47.65 mmol) and TEAB (5.00 g, 23.81 mmol) dissolved in 25 mL of 1 M H₂SO₄ were introduced. After 30 min stirring and 1 h cooling, a bright yellow–orange solid was obtained, which was isolated and dried as described above.

Tetrapropylammonium tribromide (TPATB).

Prepared as described for TEATB, except using V_2O_5 (0.06 g, 0.34 mmol) in H_2O_2 (10 mL, 88.42 mmol), and a solution of KBr (4.76 g, 40 mmol) with TPAB (4.26 g, 16 mmol) in 35 mL water. In this case, 50 mL of 1 M H_2SO_4 was added gradually, and the mixture was stirred for 2 h before isolation.

Tetrabutylammonium tribromide (TBATB).

Synthesized following the same protocol, with V_2O_5 (0.05 g, 0.27 mmol) in H_2O_2 (5 mL, 44.12 mmol), KBr (3.70 g, 31.09 mmol) and TBAB (5.00 g, 15.53 mmol) in 35 mL water, and 50 mL of 1 M H_2SO_4 . Stirring for 2 h yielded bright yellow microcrystals.

Cetyltrimethylammonium tribromide (CTMATB).

Obtained as above, except V_2O_5 (0.34 g, 0.06 mmol) was used in H_2O_2 (5 mL, 44.15 mmol), and diluted with 110 mL DI water before addition of KBr (4.89 g, 41.07 mmol) and CTMAB (5.00 g, 13.74 mmol) in 150 mL water. Subsequently, 25 mL of 1 M H_2SO_4 was introduced producing bright yellow crystalline product.

Cetylpyridinium tribromide (CetPyTB).

Prepared analogously, using V_2O_5 (0.06 g, 0.34 mmol) in H_2O_2 (5 mL, 44.12 mmol) and a solution of KBr (4.89 g, 41.07 mmol) with cetylpyridinium bromide (5.28 g, 13.74 mmol) in 35 mL water, followed by gradual addition of 50 mL of 1 M H_2SO_4 . A yellow crystalline product was obtained after 2 h stirring.

All QATB salts were obtained as stable yellow to orange solids and stored in airtight containers under dry conditions to prevent decomposition.

Bromination of graphene with different QATBs

In a typical experiment, 5 g of the desired tribromide was dissolved in 50 mL of acetonitrile, after which 250 mg of the synthesized rGO was introduced gradually under constant stirring. The suspension was sonicated for 30 min and subsequently refluxed at 90 °C for 1 h. Following natural cooling to room temperature, the reaction mixture was washed repeatedly with acetone, deionized water and ethanol to remove residual reagents. The resulting solid was dried at 60 °C to yield the brominated graphene samples. For simplicity, the products obtained using different quaternary ammonium tribromides are denoted as TEATB@rGO, TPATB@rGO, TBATB@rGO, CTMATB@rGO, and CetPyTB@rGO, corresponding to the use of TEATB, TPATB, TBATB, CTMATB, and CetPyTB, respectively.

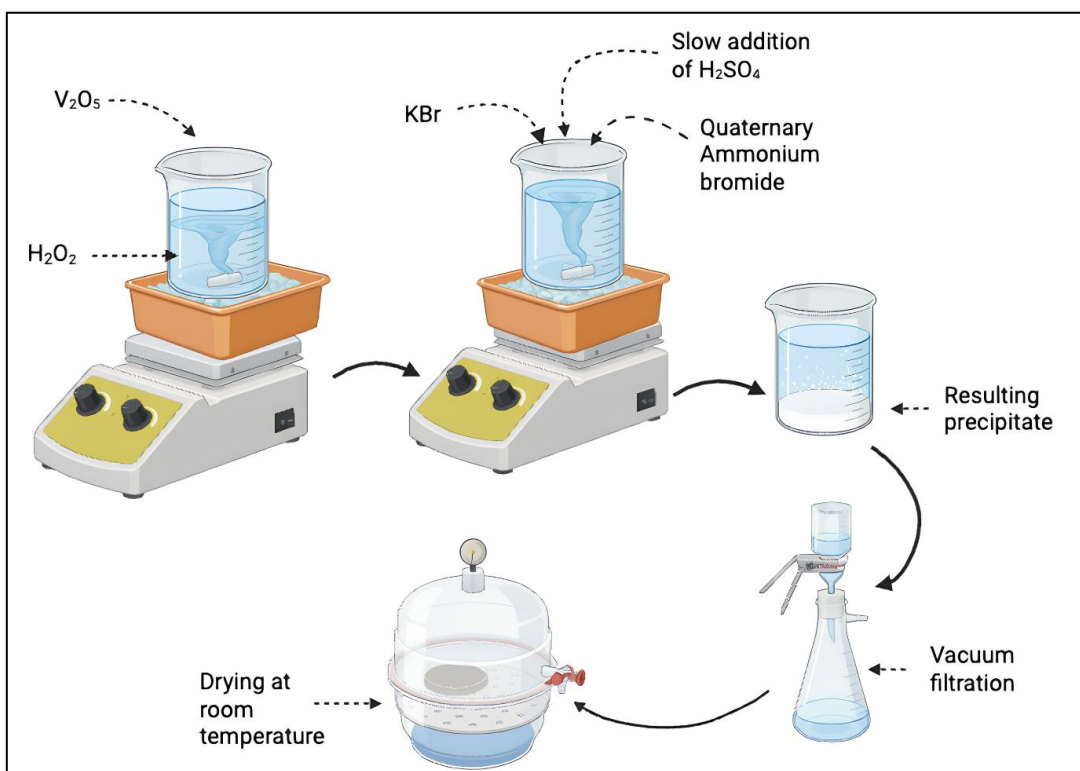


Figure 5.13. Schematic representation of synthesis of QATBs.

5.3.2 Results and discussion

FTIR spectroscopy was employed as the primary analytical tool to verify the successful bromination of rGO. The FTIR spectra of pristine rGO and the brominated samples are presented in Figure 5.14. Several characteristic peaks are observed in all samples. In all samples, the peaks observed at approximately 2930 cm^{-1} and 2875 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of $-\text{CH}_3$ groups, respectively. A relatively intense band at $\sim 1720\text{ cm}^{-1}$ corresponds to the stretching vibration of the carbonyl ($-\text{C}=\text{O}$) group, confirming the partial retention of oxygenated functionalities such as carboxylic acids and carbonyls after reduction. The presence of these groups is indicative of incomplete deoxygenation during the reduction process, a characteristic commonly observed in chemically reduced graphene oxides. The broad band centered at approximately 3437 cm^{-1} can be assigned to $-\text{OH}$ stretching vibrations associated with surface hydroxyl groups and interlayer adsorbed water molecules. The broad nature of this band signifies strong hydrogen bonding interactions. Furthermore, a moderate band near 1630 cm^{-1} corresponds to the bending mode of molecular water adsorbed on the graphene surface, indicating residual moisture entrapped within the stacked layers of rGO sheets and the characteristic $\text{C}=\text{C}$ stretching band of the graphitic structure appears around 1560 cm^{-1} . In addition, peaks observed at $\sim 1160\text{ cm}^{-1}$ and $\sim 630\text{ cm}^{-1}$ are attributed to $-\text{C}-\text{O}$ stretching and $\text{C}-\text{H}$ bending vibrations, respectively, further confirming the presence of oxygen-containing functionalities even after chemical reduction. Notable, a distinct absorption peak appears at $\sim 1068\text{ cm}^{-1}$ in the pristine rGO spectrum, which can be assigned to $\text{C}-\text{N}$ stretching vibrations. This suggests the incorporation of nitrogen atoms, likely originating from the use of NaNO_3 during the synthesis process. The presence of nitrogen functionalities in the rGO matrix is further supported by XPS and EDX analyses, as discussed in later sections [17,65].

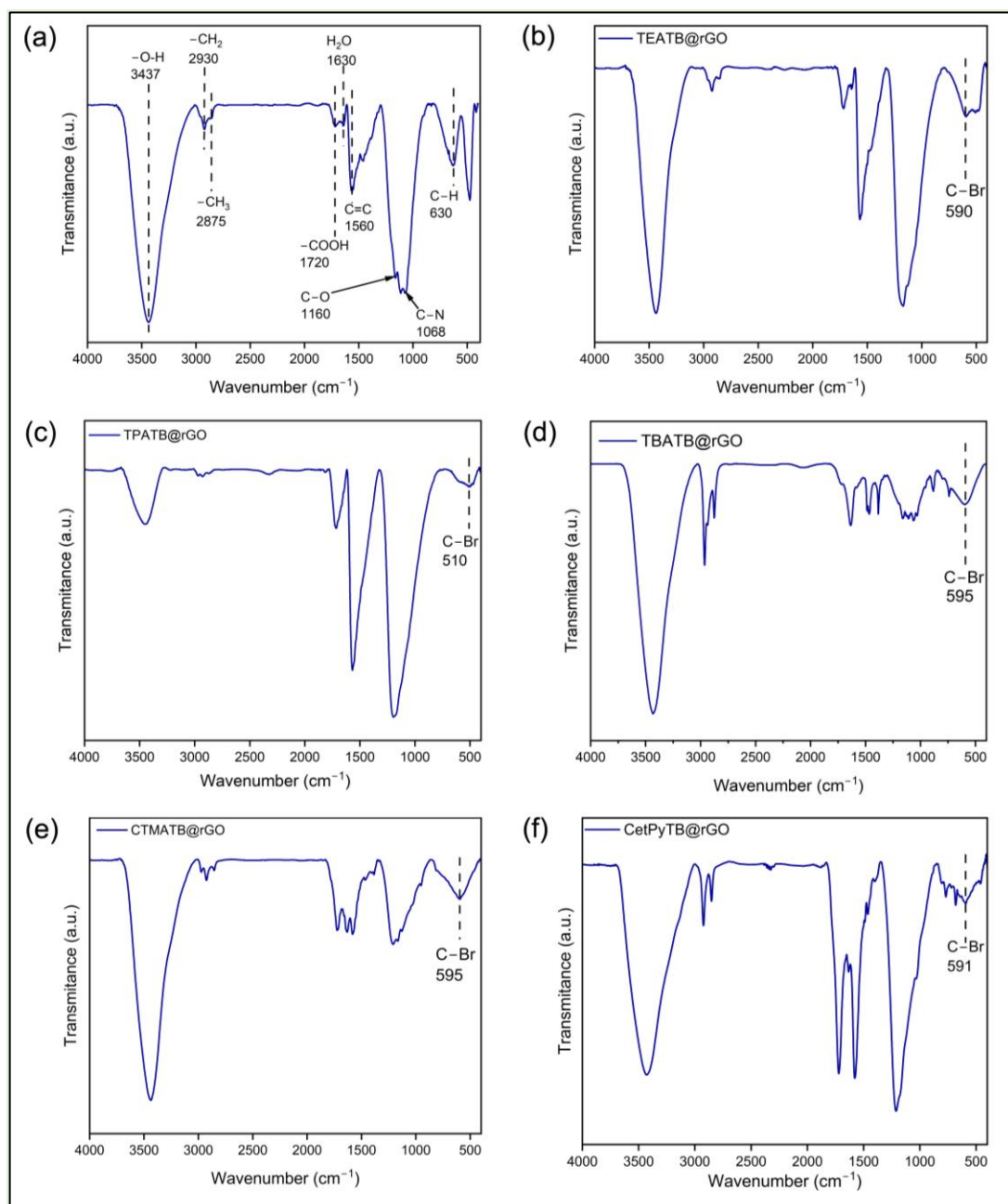


Figure 5.14. FTIR spectrum of (a) rGO (b) TEATB@rGO (c) TPATB@rGO (d) TBATB@rGO (e) CTMATB@rGO (f) CetPyTB@rGO.

Upon bromination, new peaks appear in the FTIR spectrum of all brominated samples (Figure 5.14 (b)-(f)). Most significantly, a new absorption band emerges around 590 cm^{-1} in all brominated samples, which can be unambiguously attributed to C-Br

stretching vibrations [11,25]. The presence of this band indicates successful covalent bonding of bromine atoms to the graphene framework.

X-ray diffraction (XRD) was also used to examine structural changes in rGO after bromination using the five different tribromide reagents. The XRD patterns of rGO and brominated samples are shown in Figure 5.15. The unmodified rGO, exhibited a broad (002) diffraction peak centered at approximately $2\theta=24.6^\circ$ characteristic of disordered graphitic materials. This broad peak reflects partial restacking of graphene sheets after reduction and the presence of defect sites, which are typical in chemically derived rGO materials [17].

Upon bromination using different tribromide reagents, the XRD patterns of all samples retained a similar broad reflection in the 2θ range of $24-25^\circ$, corresponding to the (002) plane of few-layer graphene. To quantify the changes, the interlayer distance and stacking height were calculated using Equations 5.11 and 5.12 respectively:

$$n\lambda = 2d\sin\theta \quad (5.11)$$

$$L_c = \frac{K\lambda}{\beta\cos\theta} \quad (5.12)$$

Where n , λ , d , L_c , K , β , represent the order of diffraction, wavelength of incident X-rays (0.15406 nm), interlayer distance, stacking height, a constant factor of 0.9 applied to the (002) peak and the FWHM in radians respectively.

The results obtained from all the equations are summarised in Table 5.8. The calculated interlayer spacing (d), determined from Bragg's law, was essentially unchanged at 0.35 –0.36 nm, in agreement with that of rGO (0.36 nm). This observation confirms that bromination does not lead to any interlayer expansion suggesting that the bromination primarily induces surface functionalization rather than intercalation of bulky species between the graphene layers.

Further, the stacking height (L_c), calculated using the Scherrer equation, ranged from 0.99 to 1.22 nm. Specifically, rGO exhibited an L_c of 1.15 nm, while the brominated

samples showed slightly lower L_C values: 1.07 nm for TPATB@rGO, 1.07 nm for TEATB@rGO, and 0.99 nm for CTMATB@rGO and CetPyTB@rGO.

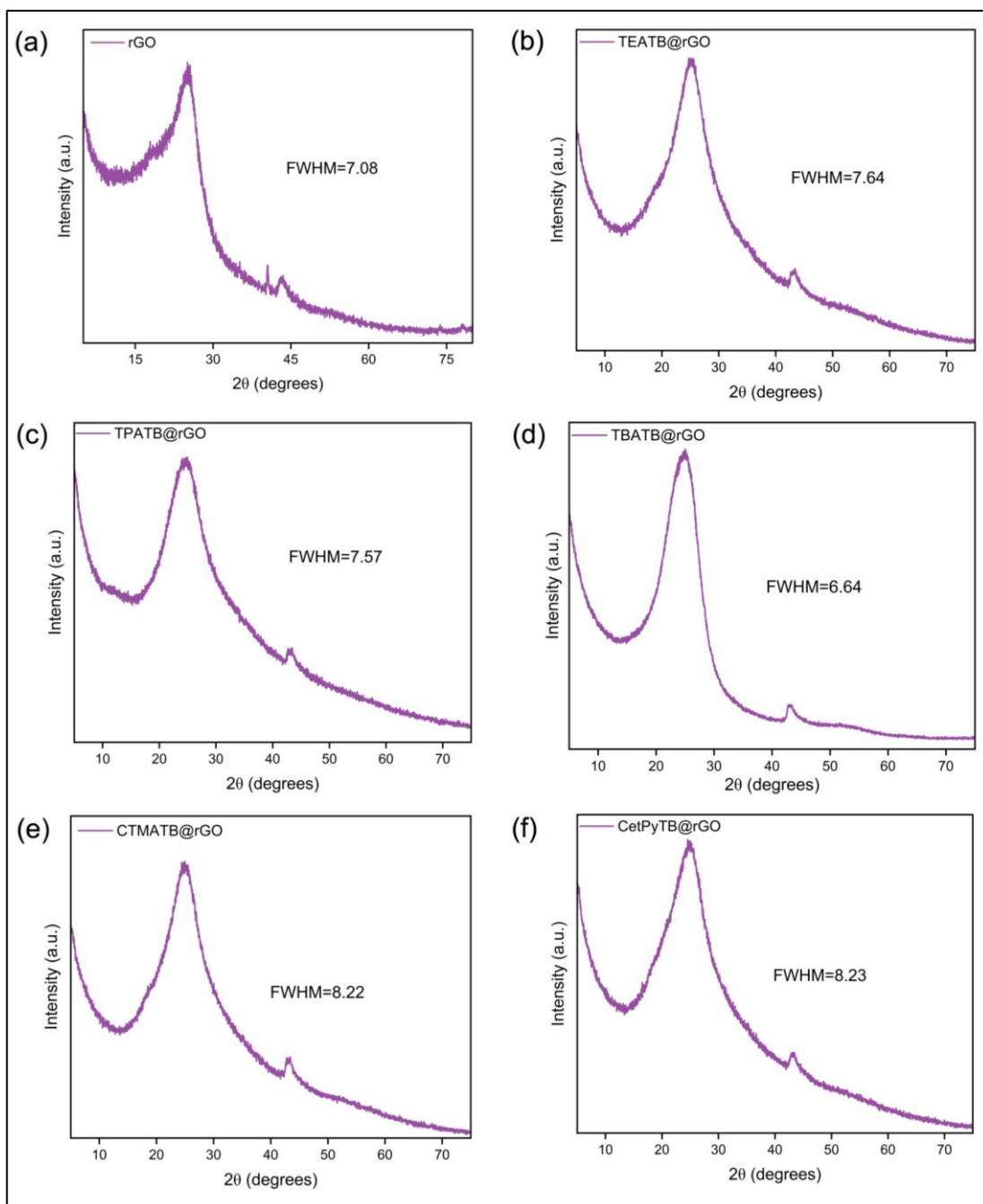


Figure 5.15. XRD spectrum of (a) rGO (b) TEATB@rGO (c) TPATB@rGO (d) TBATB@rGO (e) CTMATB@rGO (f) CetPyTB@rGO.

The exception was TBATB@rGO which showed a marginally higher value of 1.22 nm. This minor variation indicates that bromination did not lead to exfoliation or collapse of the graphene layers. Additionally, the absence of any additional reflections in the XRD patterns, indicates the absence of any intercalation compounds or impurities after bromination. Thus, XRD analysis confirms that bromination using different tribromides functionalizes the rGO's surface with minimal disruption to its layered structure, supporting a surface-modification rather than bulk-intercalation.

Table 5.8: Comparison of structural parameters of pristine rGO and brominated samples derived from XRD analysis.

Sample	Peak (002)			
	2 θ (deg)	FWHM (deg)	d (nm)	L _C
rGO	24.32	7.08	0.36	1.15
TEATB@rGO	25.08	7.64	0.35	1.07
TPATB@rGO	24.81	7.57	0.36	1.08
TBATB@rGO	24.49	6.64	0.36	1.22
CTMATB@rGO	24.82	8.22	0.36	0.99
CetPyTB@rGO	24.56	8.23	0.36	0.99

The morphology of all prepared samples was examined using scanning electron microscopy (SEM). As shown in Figure 5.16, the materials exhibited a highly exfoliated, curled and wrinkled like structure characteristic of graphene-based materials. The images revealed two-dimensional sheets with lateral dimensions ranging from several hundred nanometres to a few microns. In addition, the distribution of various elements in all samples was measured by SEM-EDS. EDS analysis revealed that the bromine content varied significantly depending on the tribromide used for functionalization (Table 5.9).

Among the samples, TPATB@rGO exhibited the highest bromine content (5.22 at%),

followed by TBATB@rGO (4.73 at%), TEATB@rGO (4.41 at%), CTMATB@rGO (3.99 wt%), and CetPyTB@rGO (1.53 at%). Interestingly, all samples also contained trace amounts of nitrogen, although nitrogen was not deliberately introduced during the bromination process. This nitrogen incorporation is likely attributed to the ammonium ions present in the tribromide salts, which may have partially reacted with the rGO surface. Furthermore, comparison of the C/O atomic ratios revealed a marked reduction in oxygen content in all brominated samples relative to pristine rGO, which initially contained approximately 17.67 at% oxygen. This decrease suggests partial removal or chemical transformation of oxygen-containing functional groups during bromination, possibly through the formation of oxybrominated species. This inference is further supported by the deconvoluted Br 3d XPS spectra, which exhibit components corresponding to Br–O bonding. Notably, no elements other than carbon, oxygen, nitrogen, and bromine were detected in the SEM–EDS analysis of all brominated samples, confirming the absence of any detectable impurities.

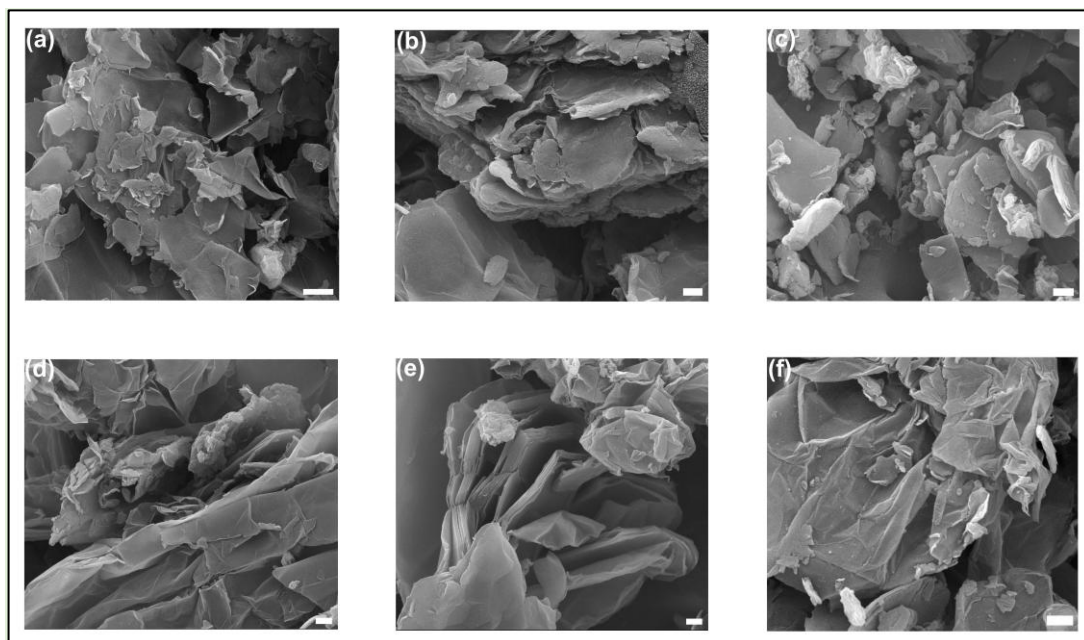


Figure 5.16. FESEM image of (a) rGO (b) TEATB@rGO (c) TPATB@rGO (d) TBATB@rGO (e) CTMATB@rGO (f) CetPyTB@rGO (scale=1 μ m).

Table 5.9: Elemental composition of all samples obtained from EDS.

Sample	Atomic % C	Atomic % N	Atomic % O	Atomic % Br	Other elements
rGO	81.13	0.22	17.67	--	Na=0.86% K=0.12%
TEATB@rGO	77.24	1.31	17.04	4.41	--
TPATB@rGO	77.21	5.65	11.92	5.22	--
TBATB@rGO	85.44	4.68	5.15	4.73	--
CTMATB@rGO	79.78	3.38	12.85	3.99	--
CetPyTB@rGO	78.84	6.04	13.60	1.53	--

XPS was further employed to examine the elemental composition and chemical bonding states of all the samples. XPS survey spectra of rGO and the brominated samples are shown in Figure 5.17 (a) and Figure 5.18 (a) respectively. The XPS spectrum of pristine rGO revealed the presence of carbon, nitrogen, and oxygen as the main elements, with carbon being the most abundant, and a minor trace of sodium also detected (Figure 5.17 (b)). The C 1s peak appeared at ~284.5 eV, N 1s at ~399.8 eV, and O 1s at ~532.0 eV, along with a weak Na 1s signal appearing near 31 eV. The presence of nitrogen and sodium, is attributed to the use of sodium nitrate during synthesis, while oxygen originates from residual oxygen-containing functional groups formed during the oxidation–reduction process. The high-resolution C 1s spectrum of rGO could be deconvoluted into five individual components (Figure 5.17 (c)). The main peak at 284.4 eV corresponds to sp^2 -hybridized C=C bonds in the graphene lattice. The peak at 286.2 eV is assigned to C–O bonds from hydroxyl or epoxy groups, whereas the component at 287.3 eV arises from carbonyl (C=O) functionalities. The peak at 288.65 eV is associated with O–C=O groups, confirming the presence of residual oxygen-containing functionalities introduced during the oxidation–reduction cycle. An additional minor peak at 290.15 eV is attributed to π – π^* shake-up satellite

features, reflecting the preserved aromatic structure of the graphene sheets. It is worth noting that although rGO contains 0.58 at.% N, no distinct C–N component could be resolved in the C 1s spectrum. This is likely because the nitrogen content is very low, and the C–N signal may only appear as a subtle shoulder buried beneath the dominant C–O or C=C peaks [66]. In contrast, all brominated samples exhibited additional Br 3d, Br 3p, Br 3s peaks at binding energies of 69 eV, 182 eV, 257 eV along with the characteristic C 1s, N 1s and O 1s peaks. The quantitative atomic percentages obtained from the survey spectra are presented in Figure 5.18 (b).

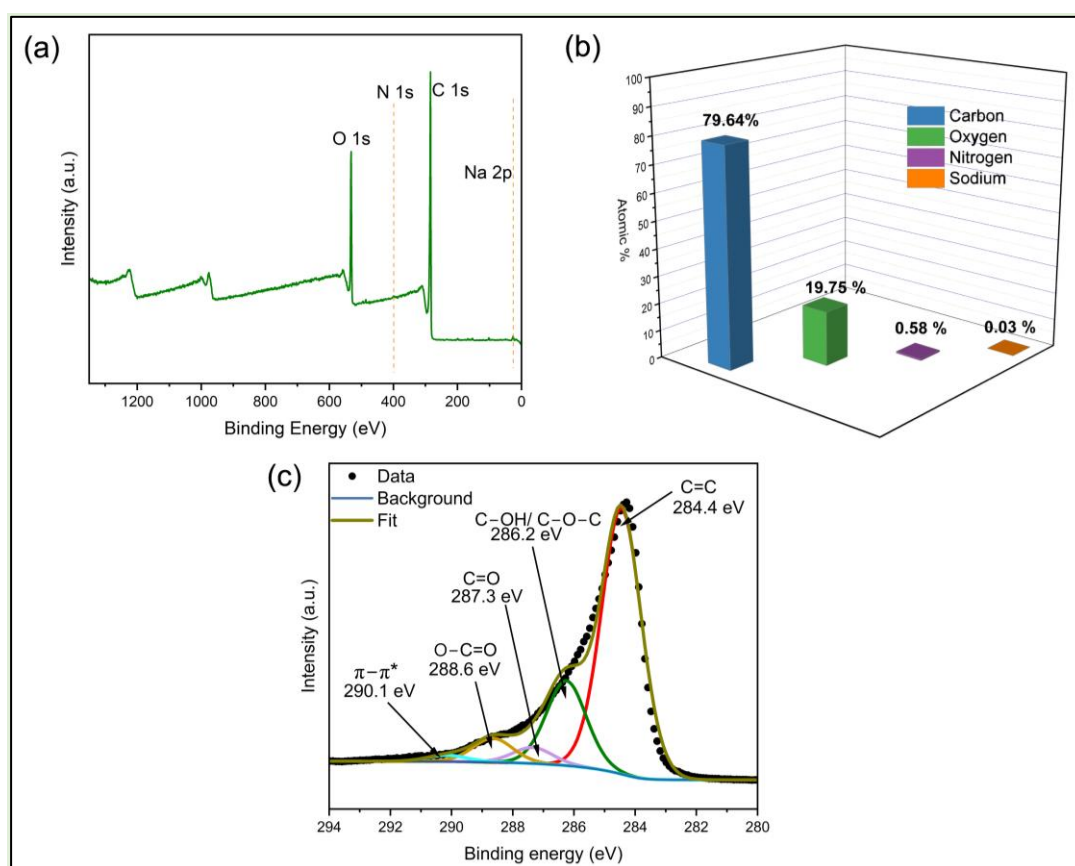


Figure 5.17. (a) XPS survey spectrum of rGO (b) Atomic concentration obtained from XPS (c) Deconvoluted HR-XPS spectrum of C1s region of rGO.

From Figure 5.18 (b), it is evident that, in addition to bromine, four of the tribromides, namely TPATB, TEATB, CTMATB, and TBATB also introduced nitrogen species into the samples, with nitrogen contents of 1.75%, 1.57%, 2.14%, and 4.68%, respectively,

which is consistent with the findings from the EDS analysis discussed earlier. This incorporation can be attributed to the presence of nitrogen in the form of ammonium ions within these tribromide salts, which likely interact with the rGO surface during bromination, leading to nitrogen incorporation into the graphene framework. In contrast, in the case of CetylPyTB, the nitrogen remains confined within the stable quaternary pyridinium ring, preventing its transfer to the graphene lattice. Further, the bromine contents in all brominated rGO samples varied significantly depending on the tribromide used, ranging from 4.73 at.% (for TBATB@rGO) to 9.38 at.% (CTMATB@rGO), indicating that the extent of bromination is strongly influenced by the nature of the tribromide used. Notably, the obtained bromine levels are significantly higher, and in some cases comparable to those reported for rGO brominated using conventional reagents such as liquid bromine or hydrobromic acid [9,11,22]. These results underscore the effectiveness of the present synthesis approach, which enables rapid and efficient bromine incorporation while utilizing an environmentally benign brominating system.

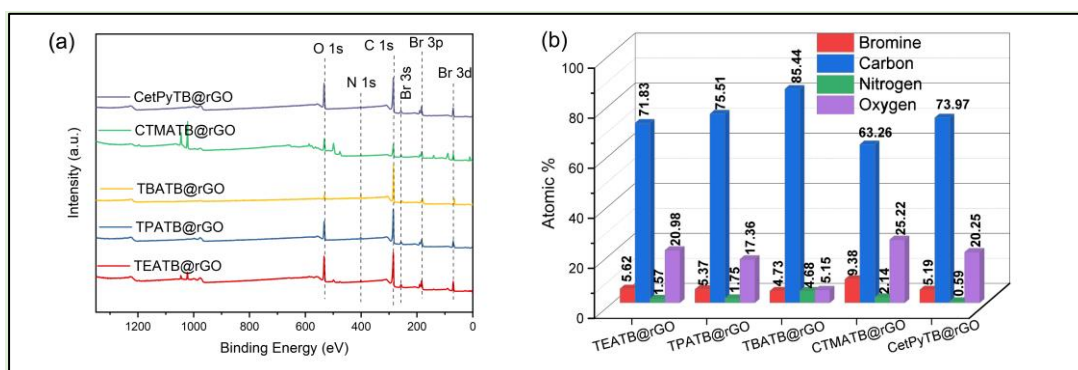


Figure 5.18. (a) XPS survey spectra of all brominated samples (TEATB@rGO, TPATB@rGO, TBATB@rGO, CTMATB@rGO and CetPyTB@rGO). (b) Atomic concentration obtained from XPS.

Deconvolution of the C 1s peak for all brominated samples (Figure 5.19 (a)–(e)) revealed an additional component at a BE of ~285.4 eV, in addition to the components

observed for rGO. This component can be attributed to the C–N and C–Br bonds as both of them have very similar binding energies[17,23]. The C–Br component is reported to have a binding energy at ~285.5 eV while the C–N bond is reported at ~285.8 eV. Hence, an unresolved single peak was obtained for both bonds. The appearance of this component provides clear evidence for successful bromination and partial nitrogen incorporation. In addition, to understand whether the bromine atoms are connected to graphene by covalent bonds or simply adhered to its surface, high resolution XPS spectra of Br 3d were also recorded and further deconvoluted as shown in Figure 5.20. The deconvolution of the Br 3d region yielded some very interesting results. Across all brominated samples, four distinct components corresponding to different bonding environments were resolved. The first component at a BE of 70.2 eV corresponds to bromine covalently attached to sp^2 and sp^3 carbon atoms. This confirms covalent attachment of bromine to the graphene framework and is consistent with the C 1s deconvolution results.

The second component at a BE of ~68.5 eV is attributed to bromine physically adsorbed onto the graphene's surface. The third and fourth components at BEs of ~68.8 eV and ~72.8 eV corresponds to $C_n \rightarrow Br_2$ surface complexes formed by charge transfer to the bromine molecule acting as electron acceptor and oxybrominated derivatives respectively. From Figure 5.20 (a)–(e), it can be seen that CTMATB@rGO demonstrated the highest level of covalently attached bromine (97.02%) followed by CetylPyTB@rGO (90.02%), TEATB@rGO (85.83%), TPATB@rGO (70.83%) and TBATB@rGO (14.44 %). In contrast, physically adsorbed Br^- was most prominent in TBATB@rGO (38.74%) followed by TEATB@rGO (9.61%) and CTMATB@rGO (2.98%). No physically adsorbed Br^- component was detected in TPATB@rGO and CetylPyTB@rGO. In terms of $C_n \rightarrow Br_2$ surface complexes, TBATB@rGO exhibited the largest area contributing to 45.81%, followed by TPATB@rGO (28.25%), CetylPyTB@rGO (9.98%) and TEATB@rGO (4.56) whereas CTMATB@rGO did

not show a component corresponding to it. Oxybrominated derivatives were absent in TEATB@rGO, CetylPyTB@rGO and CTMATB@rGO, but were observed in TPATB@rGO and TBATB@rGO, with the latter displaying the highest content (1.01%).

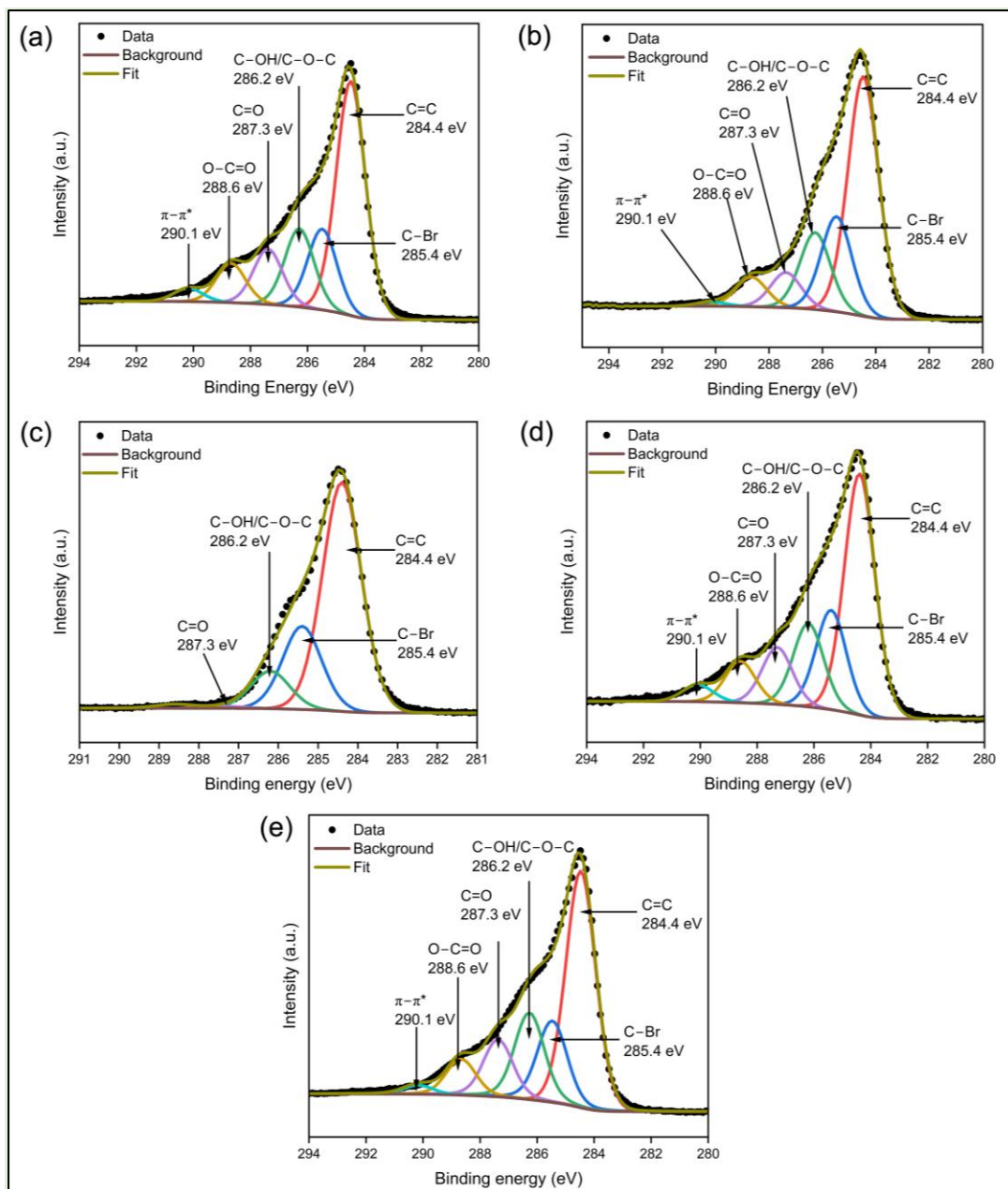


Figure 5.19. Deconvoluted HR-XPS spectrum of C1s region of (a) TEATB@rGO, (b) TPATB@rGO, (c) TBATB@rGO, (d) CTMATB@rGO and (e) CetPyTB@rGO.

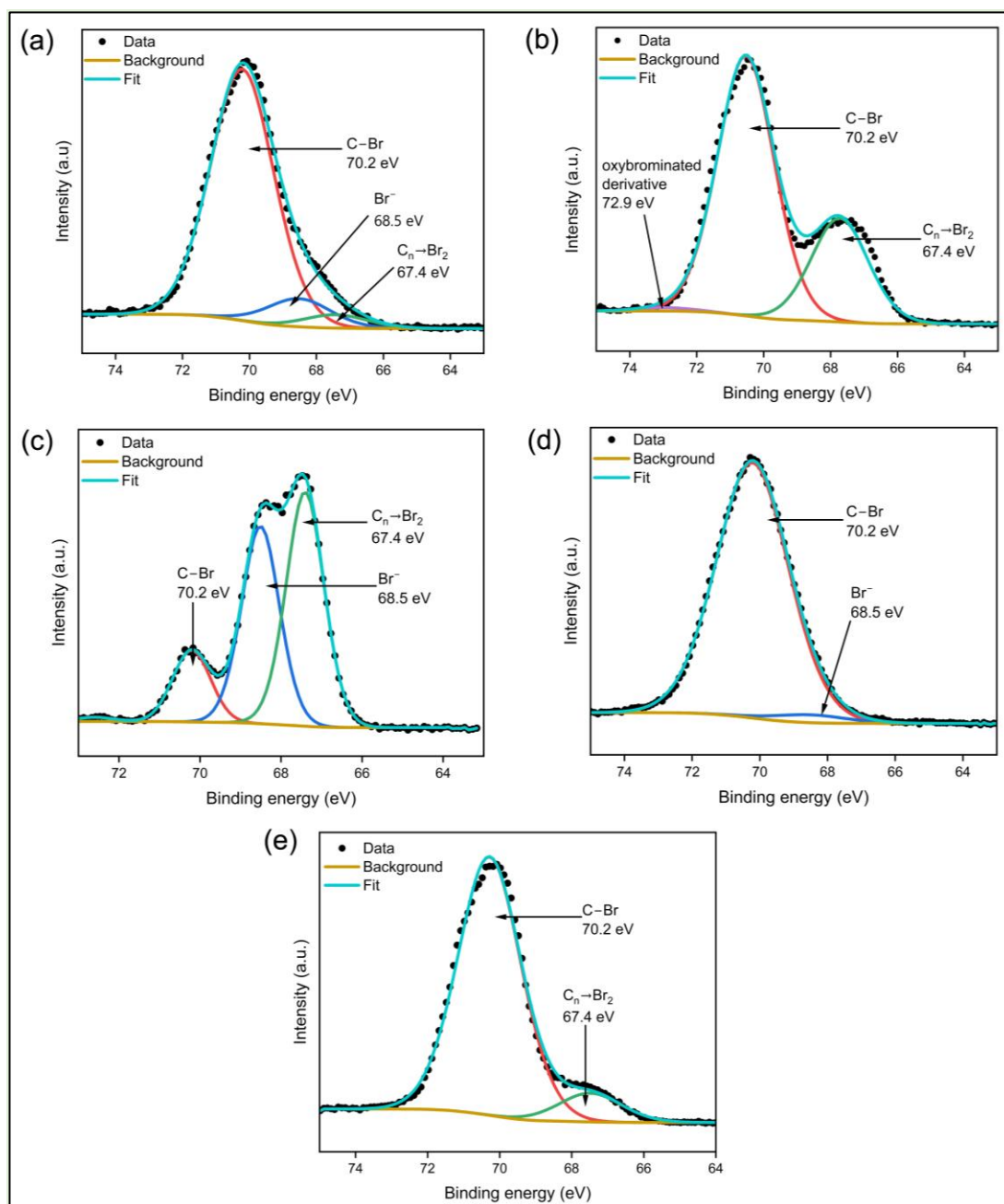


Figure 5.20. Deconvoluted HR-XPS spectrum of Br 3d region of (a) TEATB@rGO, (b) TPATB@rGO, (c) TBATB@rGO, (d) CTMATB@rGO and (e) CetPyTB@rGO.

Collectively, these XPS results confirm that bromination primary proceeds through covalent functionalization of the graphene basal plane and that the choice of tribromide reagent plays a decisive role in bromine loading. The exceptionally high fraction of covalently bonded bromine and the absence of oxybrominated species or

surface complexes in CTMATB@rGO indicate that CTMATB is the best efficient brominating agent among those tested. Conversely the presence of physically adsorbed bromine and oxybrominated derivatives together with a lower fraction of covalently attached bromine in TPATB@rGO, TEATB@rGO, CetylPyTB@rGO and TBATB@rGO reflect less efficient bromination.

Thus, based on these observations, the overall bromination efficiency of the tribromides follows the order:

CTMATB>CetylPyTB>TEATB>TPATB>TBATB

5.3.3 Conclusion

In summary, we evaluated the bromination efficiency of five environmentally benign and non-toxic tribromides, designated as TEATB, TPATB, TBATB, CTMATb and CetPyTB. Remarkably, the bromination of reduced graphene oxide (rGO) was achieved within only 60 minutes, in stark contrast to the several hours or even days typically required when using conventional brominating reagents such as liquid bromine or hydrobromic acid, which are both hazardous and yield inferior bromination levels. The resulting brominated graphene samples exhibited notable variations in bromine concentration, depending on the tribromide employed. Comprehensive characterization confirmed the successful covalent attachment of bromine atoms to the graphene framework.

XRD analysis revealed that the interlayer spacing of rGO remained essentially unchanged after bromination, indicating that bromine atoms did not intercalate between the graphene layers but were instead attached to the surface. FESEM images showed all brominated samples retained a crumpled, sheet-like morphology typical of graphene-based materials. Among them, CTMATB@rGO exhibited the highest bromine concentration (~20 wt%), as determined by EDS analysis. Further, FTIR and

XPS measurements confirmed the successful bromination achieved with all five tribromide reagents. In the FTIR spectra, the appearance of a new band near 590 cm^{-1} , corresponding to C–Br stretching vibrations, provided clear evidence of bromine incorporation. This observation was corroborated by XPS survey spectra, which displayed distinct Br 3d, Br 3p, and Br 3s peaks in all brominated samples. Moreover, deconvolution of the C 1s spectra revealed an additional component at a binding energy of $\sim 285.4\text{ eV}$, characteristic of C–Br and C–N bonding environments, confirming successful surface functionalization.

Quantitative XPS analysis showed that functionalization of rGO with TEATB, TPATB, TBATB, CTMATB, and CetPyTB yielded bromine contents of 5.62%, 5.37%, 4.73%, 9.38%, and 5.19%, respectively. In addition, since the tribromides had nitrogen containing ammonium groups, it was found that treating rGO with the tribromides also resulted in significant addition of nitrogen containing groups. It was found that samples TEATB@rGO, TPATB@rGO, TBATB@rGO, CTMATB@rGO and CetPyTB@rGO contained 1.57 %, 1.75 %, 4.68 %, 2.14 % and 0.59 % nitrogen. Additionally, deconvolution of the Br 3d spectra for all brominated samples revealed distinct variations in the bromine bonding environments, depending on the specific tribromide used. Notably, the sample CTMATB@rGO showed no oxybrominated derivatives and exhibited the highest proportion of covalently bonded bromine (97.02%), underscoring the superior bromination efficiency of CTMATB compared to the other reagents. In contrast, TPATB@rGO, TEATB@rGO, CetPyTB@rGO, and TBATB@rGO displayed 70.83%, 85.83%, 90.02%, and 14.44% covalently bonded bromine, respectively.

Thus, the tested tribromides demonstrate excellent potential as efficient, non-toxic brominating agents for graphene and potentially other materials. The resulting brominated graphenes also serve as highly versatile precursors for the synthesis of

functional graphene derivatives via their reactive C–Br sites. Covalently attached bromine atoms can be readily converted to hydroxyl or amino functionalities under alkaline conditions, or further modified through esterification and amination reactions, enabling the design of novel and interesting graphene-based materials. Additionally, the prepared materials hold significant promise for applications in electrochemical sensors, energy storage, and environmental remediation.

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Chapter 6

A 3.2 V dual-functionalized
graphene supercapacitor
with high energy density
and wide temperature
tolerance for regenerative
energy storage applications

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A 3.2 V dual-functionalized graphene supercapacitor with high energy density and wide temperature tolerance for regenerative energy storage applications

6.1 Introduction

As global efforts to mitigate climate change accelerate, the transportation sector faces mounting pressure to reduce its reliance on fossil fuels and curb greenhouse gas emissions. Electric vehicles (EVs) and hybrid electric vehicles (HEVs) have gained significant traction as sustainable alternatives to internal combustion engine vehicles due to distinctive advantages, including high efficiency, low emissions and quiet operation [1]. One of the most critical features contributing to the efficiency of these vehicles is regenerative braking—a process that recovers kinetic energy during deceleration and stores it for later use. This technology not only enhances energy efficiency but also reduces wear on mechanical braking components, extending the overall lifespan of the braking system [2]. Further, energy stored using this approach can be effectively reused for subsequent acceleration phases or to meet other energy demands of the vehicle and can significantly reduce both the vehicle's overall energy consumption and the associated environmental pollution [2].

Traditionally, chemical batteries such as lithium-ion batteries have served as the primary form of energy storage systems (ESS) in most modern EVs [1,3,4]. While lithium-ion batteries offer high energy density, they suffer from limitations such as slow charge/discharge rates, reduced efficiency at high power demands, and degradation over time due to repeated cycling [3,5]. Batteries in electric vehicles experience high stress due to rapid charging and discharging during driving and braking [5]. These shortcomings can significantly restrict the effectiveness of regenerative braking, particularly in scenarios involving frequent stops, such as urban driving [2].

Supercapacitors, or ultracapacitors, have emerged as a compelling alternative to conventional batteries in applications demanding rapid energy delivery and minimal maintenance [3,4]. Unlike batteries, supercapacitors are characterized by exceptionally high-power densities and extended cycle life, making them especially suitable for applications requiring (i) rapid bursts of energy and (ii) low-maintenance energy storage solutions [3,4]. Due to these advantages, supercapacitors are

increasingly being integrated into various technologies, including alternating current (AC) line filtering, uninterruptible power supplies, and the recuperation of regenerative braking energy (RRBE) in electric vehicles (EVs) [3,6].

Studies indicate that integrating a supercapacitor (SC) with a battery system for capturing regenerative braking energy offers multiple advantages [1,2,5]. Supercapacitors are highly capable of handling rapid charging and discharging currents and can instantly deliver peak power when needed. This makes them ideal for supporting the battery during high power demands, thereby improving vehicle acceleration and extending battery life [1]. Efficient recovery and reuse of braking energy also contribute to a noticeable increase in the vehicle's driving range. Since batteries play a crucial role in electric vehicles, they typically require thermal management systems to maintain optimal temperatures. By sharing the load with the battery, supercapacitors help reduce thermal stress, lowering the need for intensive cooling [5]. Additionally, SCs can store and discharge substantial energy rapidly without degrading their lifespan [7]. Their superior ability to absorb energy during regenerative braking further enhances overall system efficiency, making them a valuable component in electric vehicle energy management. For instance, Jamadar and Jadhav [5] reported that supercapacitors can recover up to 53% more energy during braking compared to conventional batteries and deliver peak power more efficiently during driving. This enhanced power delivery results in more consistent torque output from the motor, improving overall vehicle performance. In another report, Pipitone and Vitale [2] found that supercapacitors can be used to store regenerative braking energy even in internal combustion engine vehicles. Their findings showed energy savings of approximately 20%, with only a modest increase in vehicle weight (about 2%).

However, despite their high-power capabilities, supercapacitors typically exhibit lower energy densities (5 to 10 Wh kg⁻¹), when compared to batteries, which can reach around 100 Wh kg⁻¹ [8]. Consequently, a major focus in recent supercapacitor research has been to bridge this energy density gap. An effective approach to enhancing the energy density of a supercapacitor (SC) involves the simultaneous use of electrolytes

with a broad operating voltage window and electrodes with high capacitance [9]. To attain a broader operating voltage window (OVW), ionic and organic electrolytes capable of supporting voltages of 3.0 V or higher are generally preferred over aqueous electrolytes, which are inherently limited by their lower voltage stability [8,9]. Equally critical is the advancement of high-capacitance electrode materials, where 2D materials such as graphene have shown considerable promise owing to their large specific surface areas and superior electrochemical performance [10].

Recent advancements in supercapacitor electrode research have highlighted the growing shift from conventional carbon-based materials, towards more advanced alternatives [10]. Since the isolation of graphene via mechanical exfoliation in 2004 by Novoselov and colleagues [11], chemically synthesized graphene derivatives have garnered significant interest [7].

Furthermore, the ability to fine-tune the properties of graphene by incorporating heteroatoms or functional groups makes it a highly attractive material for energy storage applications. These modifications have been shown to greatly enhance its electrochemical performance [12,13]. In our previous study [7], we developed a one-pot, scalable synthesis method for aminated graphene and found that the introduction of amine groups resulted in a fivefold increase in specific capacitance and a sevenfold improvement in volumetric energy density compared to the non-aminated form. Additionally, the aminated graphene exhibited superior cycling stability, retaining 98% of its charge capacity, compared to 92% for its unmodified counterpart. Similar enhancements have also been reported in the literature, further validating the effectiveness of such functionalization strategies [14–18].

Building upon these considerations, we propose a novel electrode material, dual-functionalized reduced graphene oxide (DFG), comprising amino- and bromo-functionalized reduced graphene oxide for application as a high-performance electrode material in supercapacitors. This is the first report on the one pot synthesis of DFG, which is achieved through a simple, low-temperature, and environmentally benign method that avoids the use of high pressures and toxic reagents such as liquid bromine. The proposed approach enables a remarkably high degree of bromination

(~9%), the highest reported to date, within a short reaction time of just 60 minutes, alongside a substantial amination level of approximately 6%. The dual functionalization with amino and bromo groups imparts key advantages to the graphene surface, significantly enhancing its wettability and facilitating improved interaction with the electrolyte, thereby boosting its electrochemical characteristics. The unique surface chemistry of DFG contributes to its outstanding capacitive behavior, making it a promising candidate for next-generation energy storage systems.

When symmetric supercapacitors are assembled with the DFG electrodes (DFG SC) and the ionic liquid electrolyte 1-ethyl-3-methylimidazolium tetrafluoroborate, it demonstrated superior electrochemical behavior when benchmarked against state-of-the-art supercapacitor systems, due to the dual functionalization. Furthermore, these devices maintained stable operation across a wide temperature range (−15 to 80 °C) and these findings establish DFG as a highly effective and scalable electrode material. We have also investigated the self-discharge behavior of the DFG SC and demonstrated their potential as advanced electrochemical energy storage (EES) systems, particularly for capturing regenerative braking energy in electric vehicles (EVs).

6.2. Materials and experimental section

6.2.1 Materials and reagents used

Graphite (< 20 μm), sodium hydroxide pellets, and sulfuric acid (98%) were obtained from Sigma-Aldrich. Cetyltrimethylammonium bromide (99%), sodium carbonate (99.5%), potassium bromide (99.5%), potassium permanganate (99%), 1-Ethyl-3-Methylimidazolium Tetrafluoroborate (EMIM BF₄, extrapure, 97%), Acetonitrile (ACN, 99.5%) and L-Ascorbic acid (99.7%) were obtained from Sisco Research Laboratories Pvt. Ltd., India. Hydrogen peroxide (50%) was purchased from Thermo Fisher Scientific India Pvt. Ltd. The chemicals were used as received and deionized (DI) water (Resistivity 18.2 MΩ cm @ 25°C) was used during the experiment.

6.2.2 Synthesis of RG, CTMATB and DFG

Reduced graphene oxide (RG) was prepared following our previously reported procedure [7]. Briefly, 1 g of graphite powder was dispersed in 23 mL of concentrated H_2SO_4 under continuous stirring in an ice bath. Subsequently, 6 g of KMnO_4 was added slowly while maintaining the reaction temperature below 10 °C. The mixture was then heated to 35 °C and stirred for 30 min, followed by two alternating cycles of sonication and mechanical stirring (30 min each). Thereafter, 70 mL of deionized water was carefully added, and the resulting suspension was ultrasonicated for an additional 30 min. The pH of the mixture was adjusted to approximately 7 using 10 M NaOH, after which 100 mL of 1 M L-ascorbic acid was added as the reducing agent. The reaction mixture was refluxed at 90 °C for 1 h, resulting in the formation of a black precipitate. The obtained product was collected by filtration, thoroughly washed with deionized water and acetone, and finally dried under vacuum at 60 °C to obtain RG.

The green brominating agent, i.e., cetyltrimethylammonium tribromide (CTMATB) was synthesized following a procedure developed by our group [19]. In a typical synthesis, 0.057 g (0.53 mmol) of sodium carbonate (Na_2CO_3) was added to 10 mL of 50% H_2O_2 (47 mmol) and stirred at room temperature for approximately 5 min until complete dissolution, yielding a clear and colorless solution. Subsequently, a solution containing 5 g (15.53 mmol) of cetyltrimethylammonium bromide (CTMAB) and 3.7 g (31.90 mmol) of potassium bromide (KBr), both dissolved in 50 mL of deionized water, was added to the reaction mixture. Thereafter, 50 mL of 2 M H_2SO_4 was introduced dropwise, leading to the immediate formation of a precipitate. The mixture was further stirred for 1 h, during which a bright yellow solid precipitated completely. The product was collected by suction filtration using Whatman No. 40 filter paper and dried in a vacuum desiccator over self-indicating coarse silica gel. The crude product was further purified by recrystallization from acetonitrile, isolated by suction filtration, and dried under vacuum. The isolated yield of CTMATB was 7.12 g (99%).

For the synthesis of dual functionalized reduced graphene oxide (DFG), 10 g of CTMATB was dissolved in 50 mL of acetonitrile. Subsequently, 500 mg of the

synthesized RG was introduced slowly to the reaction mixture while maintaining constant stirring. Later, the solution was refluxed at 80 °C for 1 hour. After completion of the reaction, the reaction mixture was allowed to cool down naturally to room temperature and was washed multiple times with de-ionised water, ethanol and acetone. The obtained solid was then dried at 60 °C to obtain DFG.

6.2.3 Instrumentation

X-ray photoelectron spectra of RG and DFG samples were recorded using a Thermo Fisher Scientific Nexsa XPS instrument equipped with a hemispherical analyzer and an Al K α excitation source ($h\nu = 1486.6$ eV). The X-ray source was operated at a power of 72 W, and the residual pressure in the analysis chamber was maintained below 4×10^{-8} mbar during data acquisition. Raman scattering measurements were carried out at room temperature using an IndiRAM CTR300 micro-Raman spectrometer in the range of 100–4100 cm^{-1} , employing a 532 nm laser with an applied power of 5 mW and a 50 $\times$ objective lens. The microstructure of the samples was investigated by X-ray diffraction (XRD). Diffraction patterns were recorded on a PANalytical X'Pert Pro diffractometer using Cu K α radiation ($\lambda = 1.540598$ Å) over the 2θ range of 5–70°. The operating tube voltage and current were 40 kV and 40 mA, respectively. The FTIR spectra of the prepared materials were obtained using a PerkinElmer Spectrum Two FTIR spectrometer in the range of 4000–400 cm^{-1} with a spectral resolution of 1 cm^{-1} . The surface morphology was examined using field-emission scanning electron microscopy (FESEM, JEOL JSM-7900F), while the nanoscale structure was analyzed by high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F20 S-TWIN) operated at an accelerating voltage of 200 kV. The elemental composition was determined using an energy-dispersive X-ray (EDX) detector from Oxford Instruments.

6.2.4 Fabrication of coin cell type SCs

For the two-electrode configuration, a symmetric full-cell supercapacitor was assembled to evaluate the electrochemical performance, rate capability, and cycling stability of the material. The electrodes were prepared by thoroughly grinding the

active material (85 wt%), Super P carbon black (5 wt%), and poly(vinylidene fluoride) (PVDF, 10 wt%) binder in N-methyl-2-pyrrolidone (NMP) to obtain a homogeneous slurry. The slurry was then uniformly coated onto a graphite sheet current collector using the doctor-blade technique and dried in a vacuum oven at 80 °C. Subsequently, the coated graphite sheets were punched into circular electrodes with a diameter of 16 mm for coin-cell fabrication. The mass loading of active material on each electrode was approximately 1 mg. Prior to device assembly, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) was dried at 120 °C overnight and subsequently diluted with acetonitrile to prepare a 4.09 M EMIMBF₄ electrolyte solution.

CR-2032-type symmetric coin-cell supercapacitors were assembled using two identical electrodes separated by a borosilicate glass-fiber filter paper (Grade BGF52C, diameter = 19 mm). A total of 100 µL of electrolyte was added to each cell, and the assembled coin cells were crimped using a hydraulic crimper (Bat Sol) under a pressure of 100 psi for 20 s.

6.2.5 Electrochemical measurements of SCs

Electrochemical characterization was performed using a Metrohm Autolab PGSTAT 2024 electrochemical workstation at room temperature (20 °C). Electrochemical impedance spectroscopy (EIS) was carried out at the open-circuit potential by applying a sinusoidal AC perturbation of 10 mV over a frequency range spanning from 100 kHz to 10 mHz.

The specific capacitance of a single working electrode (C_{SP}) was calculated from both cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) data. From CV curves, C_{SP} was determined using the integrated area of the voltammogram according to Equation 6.1 [8,9].

$$C_{SP} = \frac{2A}{\Delta V \times m \times v} \quad (6.1)$$

where A is the enclosed area of the CV curve, ΔV is the operating potential window, m is the total mass of the electrode material, and v is the scan rate. From GCD profiles, the specific capacitance was evaluated using Equation 6.2 [8,9].

$$C_{SP} = \frac{2(I \times \Delta t)}{m \times \Delta V} \quad (6.2)$$

where I denotes the applied discharge current and Δt is the discharge time.

The energy density (E_d , Wh kg⁻¹) and power density (P_d , W kg⁻¹) of the assembled supercapacitor devices were calculated from the charge–discharge characteristics using the following relations [7–9]:

$$E_d = \frac{1}{2 \times 4} \frac{C_{SP} \times V^2}{3.6} \quad (6.3)$$

$$P_d = \frac{E_d}{\Delta t} \times 3600 \quad (6.4)$$

The temperature-dependent electrochemical performance of the DFG supercapacitor was evaluated by subjecting the device to controlled environments, including heating in an electric oven over the temperature range of 20–100 °C and cooling in a freezer at –15 °C.

6.3 Results and discussion

6.3.1 Material characterization

The DFG was prepared by dissolving the brominating agent CTMATB in acetonitrile, followed by the addition of RG and refluxing the mixture at 80 °C. CTMATB unlike other brominating reagents such as liquid bromine exists as a stable, crystalline tribromide salt that functions as a controllable reservoir of tribromide anion (Br_3^-). Initially, when CTMATB is dissolved in acetonitrile, it breaks down into its corresponding ions i.e., $CTMA^+$ and Br_3^- and the chemical reactivity of CTMATB is governed by the dynamic equilibrium of the tribromide anion (Br_3^-), which reversibly dissociates in solution to generate low, regulated concentrations of molecular bromine ($Br_3^- \rightleftharpoons Br_2 + Br^-$). Thus, the electrophilic bromine species generated in situ preferentially interact with electron-rich sp² carbon domains of RG, particularly at defect sites, edges, and regions adjacent to residual oxygen functionalities. Rather than proceeding via classical molecular electrophilic aromatic substitution, bromination may occur through electrophilic addition or substitution-like reactions on the

heterogeneous graphene lattice, leading to the formation of covalent C–Br bonds. Further, the nitrogen species present in the CTMA⁺ chain gets attached and is responsible for the introduction of nitrogen moieties on the graphene's surface which finally resulted in the formation of DFG.

The successful dual functionalization of RG was first evaluated using FTIR spectroscopy, and the FTIR spectra of RG and DFG are presented in Figure 6.1 (a). The FTIR spectrum of RG displays characteristic features arising from residual oxygen-containing functionalities as well as the carbon framework. In the low-frequency region, a band is observed at $\sim 560\text{ cm}^{-1}$ which can be attributed to an alkene skeletal rocking vibration, originating from coupled out-of-plane deformation of the carbon framework [20]. The presence of a band at 1103 cm^{-1} , corresponds to C–O stretching vibrations, indicates that alkoxy/epoxy-type oxygen functionalities remain in RG, which is a common characteristic of chemically exfoliated graphene materials [21]. A distinct absorption band is observed at 1498 cm^{-1} which is due to aromatic ring C=C skeletal vibrations [21]. The feature at $\sim 1631\text{ cm}^{-1}$ is associated with bending vibrations of adsorbed water molecules, while the bands at 2862 and 2927 cm^{-1} arise from symmetric and asymmetric C–H stretching vibrations of $-\text{CH}_2$ groups, respectively [22–24]. Additionally, the broad absorption centered at $\sim 3437\text{ cm}^{-1}$ is attributed to O–H stretching vibrations of surface hydroxyl groups [20,24].

Upon dual functionalization to form DFG, the FTIR spectrum exhibits several new features, clearly indicating successful chemical modification. Most notably, a band at $\sim 596\text{ cm}^{-1}$ emerges which can be attributed to C–Br stretching vibrations [20,24]. Thus, providing direct evidence for the incorporation of bromine moieties onto the graphene surface. Furthermore, new absorption bands at 951 and 1164 cm^{-1} appear, which are associated with C–N stretching vibrations, with the lower-frequency band also overlapping with CH_3 rocking modes [7,20]. The appearance of an additional band at $\sim 1581\text{ cm}^{-1}$, assigned to N–H scissoring vibrations, further confirms the successful introduction of amine functionalities [7,20,25]. Collectively, the emergence of these new bands confirms that the dual functionalization strategy effectively introduces both bromine and amine groups onto the RG framework. In addition, the persistence of bands at 1127 and 1207 cm^{-1} , which fall within the C–O stretching

region, indicates that oxygen-containing functionalities coexist even after functionalization [7,20]. The bands at 1384 and 1401 cm^{-1} correspond to symmetric and asymmetric $-\text{CH}_3$ deformation vibrations, respectively, while the absorption at $\sim 1465 \text{ cm}^{-1}$ is attributed to asymmetric C–H bending of $-\text{CH}_3$ groups [20]. Similar to RG, the band observed at $\sim 1632 \text{ cm}^{-1}$ in DFG arises from bending vibrations of adsorbed water molecules [22]. A detailed assignment of all observed FTIR bands is summarized in Table 6.1.

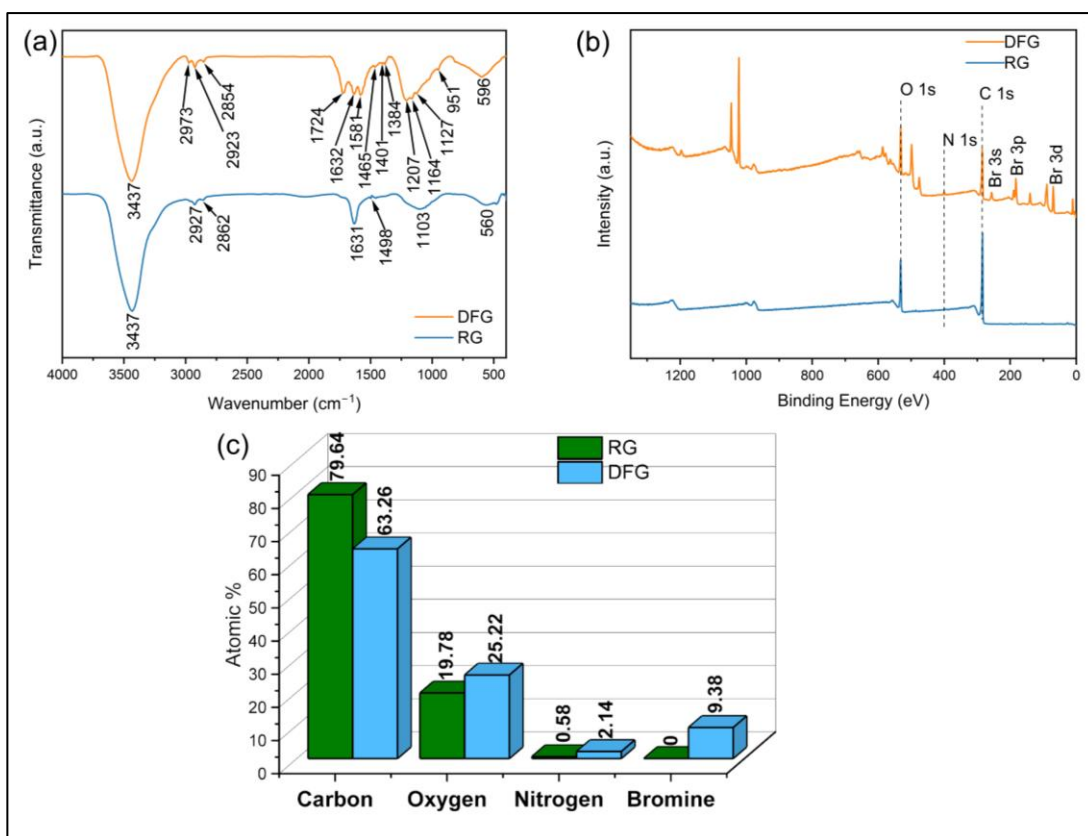


Figure 6.1. (a) FTIR Spectra of RG and DFG. (b) XPS survey spectra of RG and DFG. (c) Atomic percentages of different elements determined from XPS analysis.

Table 6.1: FTIR peaks and their corresponding functional groups for RG and DFG.

Sample	Wavenumber (cm^{-1})	Assignment	Ref.
RG	560	Alkene skeletal rocking vibration	[20]

	1103	C–O stretching	[21]
	1498	Aromatic ring C=C skeletal vibration	[20]
	1631	Adsorbed H ₂ O bending	[22]
	2862	Symmetric C–H stretching (–CH ₂)	[23,24]
	2927	Asymmetric C–H stretching (–CH ₂)	[23,24]
	3437	O–H stretching of hydroxyl groups	[20,24]
DFG	596	C–Br stretching	[20,24]
	951	C–N stretching	[7,20]
		CH ₃ rocking	
	1127	C–O stretching	[7,20]
	1164	C–N stretching	[7,20,25]
	1207	C–O stretching	[7,20]
	1384	Symmetric –CH ₃ deformation	[20]
	1401	Asymmetric –CH ₃ deformation	[20]
	1465	Asymmetric C–H bending (–CH ₃)	[20]
	1581	N–H scissoring	[7,20,25]
	1632	Adsorbed H ₂ O bending	[22]
	1724	C=O stretching (carbonyl/carboxyl groups)	[7,22]
	2854	Symmetric –CH ₂ stretching	[20,23,24]
	2923	Asymmetric –CH ₂ stretching	[20,23,24]
	2973	Asymmetric –CH ₃ stretching	[20,23,24]
	3437	O–H stretching of hydroxyl groups	[7,20]

X-ray photoelectron spectroscopy (XPS) was further employed to analyze the elemental composition and chemical bonding states of RG and DFG. The survey spectra of RG and DFG are presented in Figure 6.1 (b). The RG survey spectrum indicates the presence of carbon, nitrogen, and oxygen, with carbon being the predominant element. The characteristic C 1s, N 1s, and O 1s peaks appear at binding energies of approximately 284.5 eV, 399.8 eV, and 532.0 eV, respectively [7]. The detected nitrogen originates from the use of sodium nitrate during synthesis, while oxygen is attributed to residual oxygen-containing functional groups remaining after the oxidation–reduction process. In contrast, the DFG survey spectrum exhibits additional Br 3d, Br 3p, and Br 3s peaks at binding energies of approximately 69 eV, 182 eV, and 257 eV, respectively, alongside the C 1s, N 1s, and O 1s signals, confirming successful bromine incorporation. The quantitative atomic compositions derived from the survey spectra are summarized in Figure 6.1 (c). Notably, in addition to bromination, CTMAB introduces nitrogen species into the graphene framework, leading to an increase in nitrogen content from 0.58 at.% in RG to 2.14 at.% in DFG. These results confirm the successful dual functionalization of RG with nitrogen- and bromine-containing groups, resulting in the formation of DFG.

To gain deeper insight into the bonding configurations of the incorporated species and to differentiate between covalent functionalization and physical adsorption, high-resolution C 1s, Br 3d, and N 1s XPS spectra were recorded and deconvoluted. The high-resolution C 1s spectrum of RG can be deconvoluted into five components (Figure 6.2 (a)). The dominant peak at 284.4 eV corresponds to sp^2 -hybridized C=C bonds of the graphene lattice [23].

The peak at 286.2 eV is assigned to C–O bonds arising from hydroxyl or epoxy groups, while the component at 287.3 eV arises from carbonyl (C=O) functionalities. The peak at 288.65 eV corresponds to O–C=O groups, while a weak feature at 290.15 eV is attributed to π – π^* shake-up satellite features, indicating the preservation of aromatic conjugation within the graphene sheets [25,26]. Although RG contains 0.58 at.% nitrogen, no distinct C–N contribution could be resolved in the C 1s spectrum, most likely due to the low nitrogen concentration, with the corresponding signal appearing

as a subtle shoulder overlapping with the dominant C=C or C–O components [27].

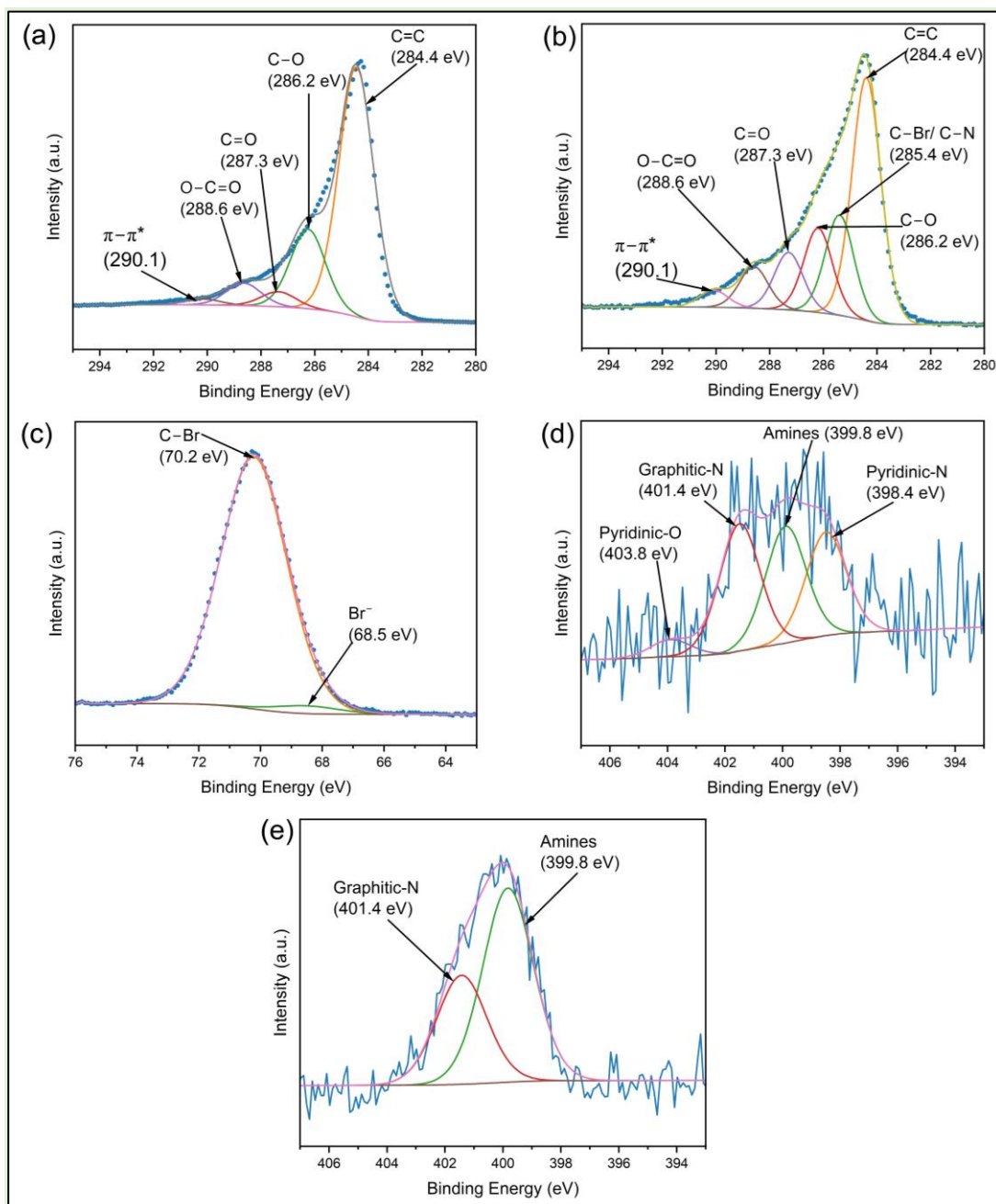


Figure 6.2. Deconvoluted HR-XPS spectra of C 1s region of (a) RG, (b) DFG. Deconvoluted HR-XPS spectra of C 1s region of (c) Br 3d. Deconvoluted HR-XPS spectra of N 1s region of (d) RG and (e) DFG.

In the case of DFG, the C 1s spectrum exhibits all the components observed for RG, along with an additional feature centered at approximately 285.4 eV (Figure 6.2 (b)).

This component is attributed to overlapping contributions from C–N and C–Br bonds, as both possess very similar binding energies. Previous reports assign C–Br and C–N bonds to ~285.5 eV and ~285.8 eV, respectively, resulting in an unresolved combined peak [7,28]. The emergence of this component provides clear evidence for the successful incorporation of both nitrogen and bromine containing functionalities into the graphene framework.

Similarly, the high-resolution Br 3d spectra of DFG was deconvoluted to determine whether bromine is covalently bonded to graphene or merely physisorbed on the surface, as shown in Figure 6.2 (c). The Br 3d region can be fitted into two distinct components corresponding to different chemical environments. The dominant component at a binding energy of 70.2 eV is attributed to bromine covalently bonded to sp^2/sp^3 carbon atoms, confirming covalent bromination of the graphene lattice and corroborating the C 1s analysis. The second component at ~68.5 eV corresponds to physically adsorbed bromine species on the graphene surface [28]. Quantitative analysis of the integrated peak areas reveals that approximately 97.02% of the bromine exists in a covalently bonded state, while only 2.98% is present as physisorbed Br^- species. In addition, high-resolution N 1s spectra of RG and DFG were also recorded and deconvoluted to elucidate the chemical states and bonding configurations of nitrogen species as shown in Figure 6.2 (d) and (e) respectively. The high-resolution N 1s spectrum of RG can be deconvoluted into four components located at binding energies of 398.4 eV, 399.87 eV, 401.4 eV, and 403.8 eV, corresponding to pyridinic-N, amine-type nitrogen, graphitic-N, and pyridinic-O species respectively [7,23,29,30]. Following functionalization, the N 1s spectrum of DFG can be fitted using only two components, assigned to amine-type nitrogen and graphitic-N. Quantitative analysis shows that the contribution of amine-type nitrogen increases significantly from 32.02% in RG to 64.05% in DFG, while graphitic-N exhibits a slight increase from 34.89% to 35.95%. This pronounced enrichment of amine-type nitrogen indicates that functionalization predominantly introduces amine functionalities, in addition to the covalent bromine incorporation discussed above. Thus, the XPS results confirm successful dual functionalization of RG with both bromine and amine functionalities which is consistent with the FTIR results.

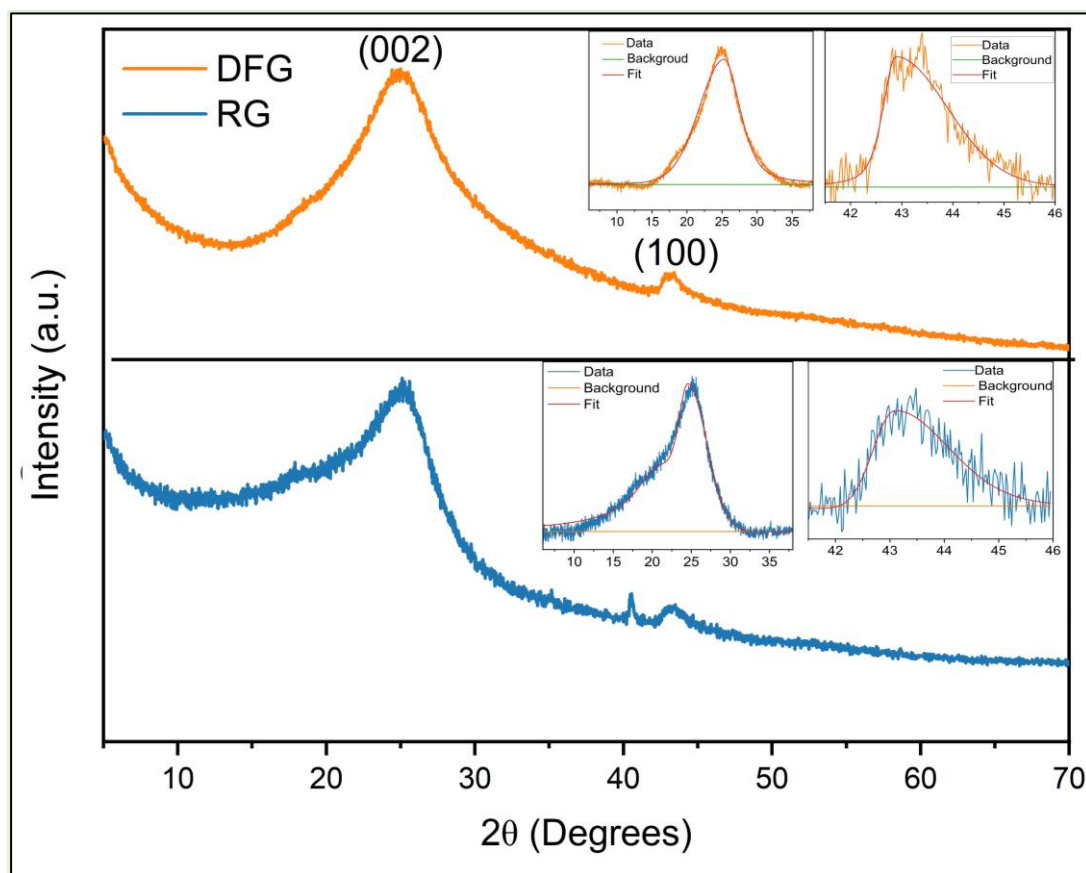


Figure 6.3. XRD spectra of RG and DFG, with insets showing the fitted (002) and (100) peaks.

X-ray diffraction (XRD) was also employed to investigate the structural changes of RG upon functionalization. The XRD patterns of RG and DFG are shown in Figure 6.3. The XRD diffraction peaks were fitted using the Fityk software to accurately extract peak positions, full width at half maximum (FWHM), and related parameters [31]. Among the available fitting functions, the split pseudo-Voigt profile implemented in Fityk provided the best agreement with the experimental data. Both samples exhibit a broad (002) diffraction peak centered at $2\theta \approx 24.73^\circ$ and 25.28° for RG and DFG, which is characteristic of disordered graphitic carbon. This broad feature arises from diffraction by short-range-ordered graphene layers, along with contributions from amorphous sp^3 -hybridized carbon domains, a behavior typical of defective or turbostratic carbon materials [8]. The peak broadening reflects partial restacking of graphene layers, as well as the presence of abundant defect sites, both of which are characteristic of chemically derived graphene materials [7]. To

quantitatively evaluate the structural changes, the interlayer spacing (d), crystallite stacking height (L_C) and lateral crystallite size (L_a) were calculated using Equations 6.5, 6.6 and 6.7, respectively [8,32].

$$n\lambda = 2d\sin\theta \quad (6.5)$$

$$L_C = \frac{0.89 \times \lambda}{\beta_{002} \times \cos\theta_{002}} \quad (6.6)$$

$$L_a = \frac{1.84 \times \lambda}{\beta_{100} \times \cos\theta_{100}} \quad (6.7)$$

Where n , λ , β_{002} , $\cos\theta_{002}$, L_a , β_{100} and $\cos\theta_{100}$ represent the order of diffraction, wavelength of incident X-rays (0.15406 nm), full width at half maximum (FWHM) of the (002) peak (in radians), Bragg angle (in radians) corresponding to (002) plane, FWHM of the (100) peak (in radians) and corresponding Bragg angle (in radians) of the (001) peak respectively. The structural parameters calculated using these equations are summarized in Table 6.2. The calculated interlayer spacing (d), determined from Bragg's law, was essentially unchanged at 0.35–0.36 nm. This observation confirms that functionalization does not result in interlayer expansion, suggesting that the introduced functional groups are confined to the surface of the graphene sheets rather than intercalated within the graphene stacks.

Table 6.2: Comparison of structural parameters of RG and DFG derived from XRD analysis.

Sample	Peak (002)				Peak (100)		
	2θ (deg)	FWHM (deg)	d (nm)	L_C (nm)	2θ (deg)	FWHM (deg)	L_a (nm)
RG	24.73	5.22	0.36	1.54	42.88	1.50	11.62
DFG	25.28	6.98	0.35	1.15	43.10	1.64	10.61

Further, L_C derived from the (002) reflection, decreases from 1.54 nm for RG to 1.15 nm for DFG, indicating reduced coherent stacking of graphene layers after functionalization. Similarly, L_a calculated from the (100) reflection, decreases from 11.62 nm to 10.61 nm upon functionalization. These reductions may be attributed to

the fragmentation of sp^2 graphitic domains caused by partial conversion of sp^2 carbon to sp^3 -hybridized sites, along with an increased density of defects. Additionally, the absence of any additional reflections in the XRD patterns, indicates the absence of any impurities formed during the functionalization process.

Raman spectroscopy was used to obtain further insight into the macroscopic structural characteristics of RG and DFG. The corresponding Raman spectra, shown in Figure 6.4 (a), display prominent D and G bands located at approximately 1350 and 1585 cm^{-1} , respectively. In addition, both samples exhibit a second-order 2D band around 2700 cm^{-1} and a combination D+G band centered near 2930 cm^{-1} [8]. The G and 2D bands arise from the first- and second-order Raman-active E_{2g} phonon modes, originating from the in-plane vibration of sp^2 -hybridized carbon atoms [33]. In contrast, the D band originates from the A_{1g} breathing mode of sp^2 carbon rings and becomes Raman-active in the presence of defects. Its pronounced intensity reflects substantial disruption of the graphene basal plane induced during graphite oxidation and exfoliation, which generates a high density of structural defects [34]. The broad feature observed around $\sim 2930\text{ cm}^{-1}$ can be assigned to second-order combination modes (D+G) and arises from the combination of two phonons with different momenta and requires a defect for its activation [35,36].

Conventionally, the intensity ratio of the D and G bands (I_D/I_G) is an effective parameter for evaluating the defect density in graphene-based materials [37,38]. However, for chemically exfoliated materials such as graphene oxide and reduced graphene oxide, this simplistic interpretation becomes unreliable due to the overlap of additional bands (D', D'', and D*) with the conventional D and G bands [37]. Thus, the direct application of raw D- and G-band intensities may not accurately capture the true extent of structural disorder. Claramunt et al. [34] demonstrated that a more accurate assessment of defect density can be achieved by deconvoluting the Raman spectra and calculating I_D/I_G using fitted peak intensities rather than raw spectral data. Lee et al. [39] demonstrated that the Raman spectra of graphene derivatives can be reliably fitted using five Lorentzian line shapes, corresponding to the D*, D, D'', G, and D' bands.

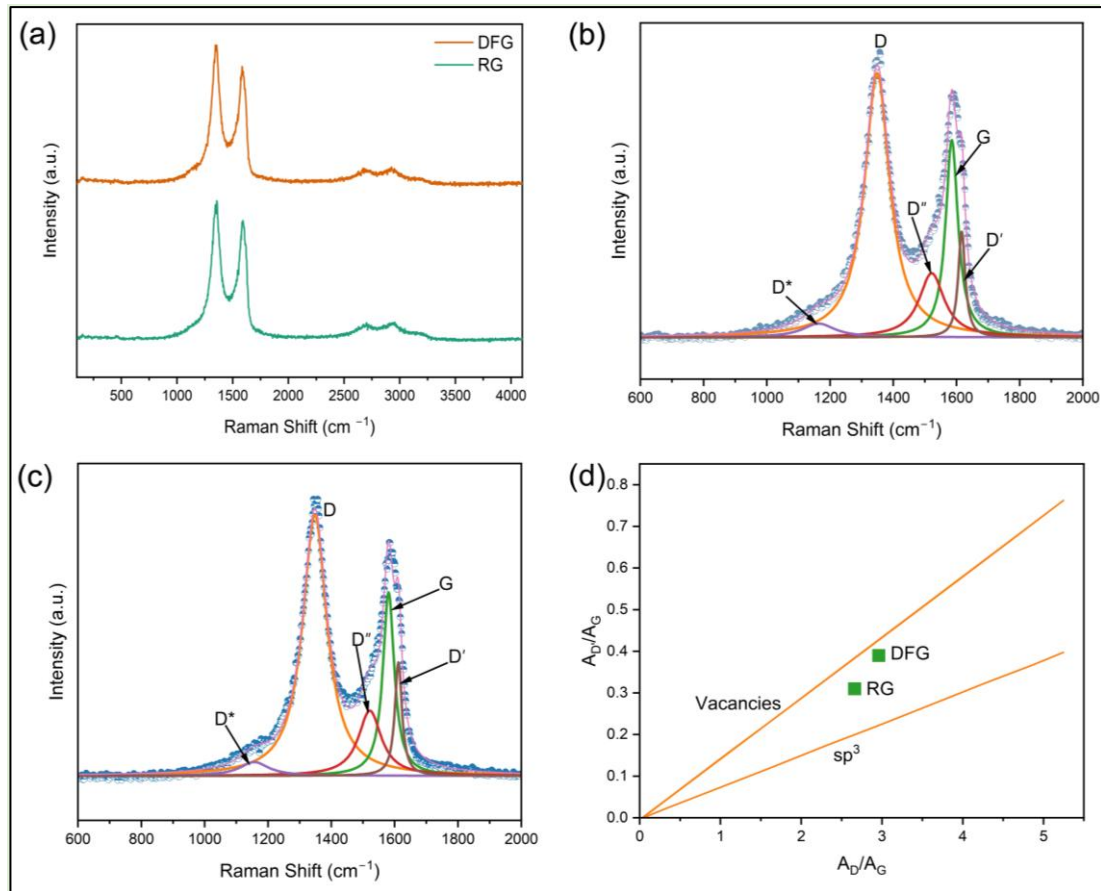


Figure 6.4. (a) Raman spectrum of RG and DFG. Fitted Raman spectra of (b) RG (c) DFG. (d) Relationship between the relative intensity of the D' band (calculated from integrated area) and the D band for RG and DFG. The solid lines indicate linear fitting of the experimental results.

Consistent with these findings, our analysis shows that Lorentzian functions provide a better fit for these five components. Accordingly, the Raman spectra of RG and DFG in the range of 600–2000 cm⁻¹ were deconvoluted using five Lorentzian peaks, as shown in Figure 6.4 (b) and (c). The bands observed at ~1620 cm⁻¹ (D'), 1500–1550 cm⁻¹ (D''), and 1150–1200 cm⁻¹ (D*) are associated with disorder-induced phonon modes. The D' band is related to intravalley scattering from lattice defects, the D'' band is commonly attributed to amorphous carbon phases, and the D* band is linked to disordered graphitic structures involving sp²–sp³ bonding [34,37]. Accordingly, this fitting-based approach was adopted in the present study, and the extracted parameters are summarized in Table 6.3.

Table 6.3: I_D , I_G , I_D/I_G and average crystallite size calculated using Raman spectroscopy.

Sample	I_D	I_G	I_D/I_G	L_a (nm)
RG	1261.15	941.05	1.340	14.3
DFG	584.63	411.28	1.421	13.5

In graphene-based materials, an increase in the I_D/I_G ratio is commonly associated with enhanced structural disorder resulting from the introduction of sp^3 -hybridized defects, functional groups, and lattice distortions [40]. In the present study, the I_D/I_G ratio increases from 1.340 for RG to 1.421 for DFG, which can be ascribed to the covalent incorporation of Br and $-NH_2$ functional groups. These functionalities locally disrupt the sp^2 carbon framework, generating additional defect sites that promote intervalley scattering and thereby intensify the D band relative to the G band. Furthermore, the I_D/I_G ratio can be employed to estimate the average crystallite size (L_a), which represents the defect-free domains within the graphene structure, using Equation 6.8 proposed by Cançado et al. [41]:

$$L_a = 2.4 \times 10^{-10} \lambda_{laser}^4 (I_G/I_D) \quad (6.8)$$

Where, λ_{laser} denotes the laser excitation wavelength. Using a 532 nm laser, the calculated L_a values were approximately 14.3 nm for RG and 13.5 nm for DFG. The reduced L_a value observed for DFG indicates a higher degree of structural disorder and defect density induced by chemical functionalization, in good agreement with previous literature reports [34,40]. Additionally, the estimated L_a values corroborate the small lateral dimensions of the aromatic domains derived from XRD analysis.

Moreover, Del Corro et al. [42] demonstrated that the relative intensities of the D and D' Raman bands can be used to distinguish different types of defects in graphene-based materials, such as sp^3 -type defects, vacancy-like defects, and grain boundaries. Subsequently, López-Díaz and co-workers extended this approach to graphene oxides,

showing that the correlation between the D and D' band intensities remains valid for chemically derived graphene systems and can be used to identify the dominant defect type [37].

According to a classification proposed by Ferrari and Robertson, graphene-based materials follow a two-stage evolution with increasing defect density [43]. In Stage 1, corresponding to low to moderate disorder, the D and D' band intensities scale with defect concentration, and their relative intensities reflect the nature of the defects, whereas in Stage 2 this relationship becomes complicated [37,43]. Cançado et al. [35] described that the transition from Stage 1 to Stage 2 disorder in graphene-based materials is governed by the progressive reduction of the distance between defects (L_D) with stage-2 disorder emerging when L_D approaches $\sim 2\text{--}3$ nm, leading to a breakdown of the Tuinstra–Koenig relation. Considering this, L_D was estimated using Equation 6.9 and the peak intensity ratio I_D/I_G . The obtained L_D values were ~ 10.37 nm for RG and ~ 10.06 nm for DFG, indicating that both samples lie within the Stage-1 disorder regime characterized by a low defect density.

$$L_D^2 \text{ (nm}^2\text{)} = (1.8 \pm 0.5) \times 10^{-9} \lambda_{laser}^4 (I_D/I_G)^{-1} \quad (6.9)$$

Accordingly, a correlation plot was constructed using the ratios of the integrated Raman band areas (denoted as A_x) to represent band intensities, as the integrated area under each band reflects the probability of the complete Raman scattering process (Figure 6.4 (d)). Previous studies have shown that, in Stage-1 graphene, vacancy-type defects are characterized by an $A_{D'}/A_D$ value of ~ 0.143 , whereas sp^3 -type defects have a value of ~ 0.077 [37,42]. In the present study, $A_{D'}/A_D$ values of 0.116 and 0.132 were obtained for RG and DFG, respectively. These values lie closer to the characteristic range of vacancy-type defects, indicating that vacancies are the dominant defect species in both samples. Furthermore, the higher $A_{D'}/A_D$ value observed for DFG suggests that vacancy-type defects become more pronounced upon functionalization.

The morphological features of DFG were also investigated using field-emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HR-TEM). The FESEM images (Figure 6.5 (a)–(b)) reveal that DFG exhibits a thin, lamellar sheet-like morphology with pronounced crumpling and corrugation at several locations. The basal planes extend over lateral dimensions of a few micrometers, indicating effective exfoliation while maintaining the structural integrity of the graphene framework [25,44].

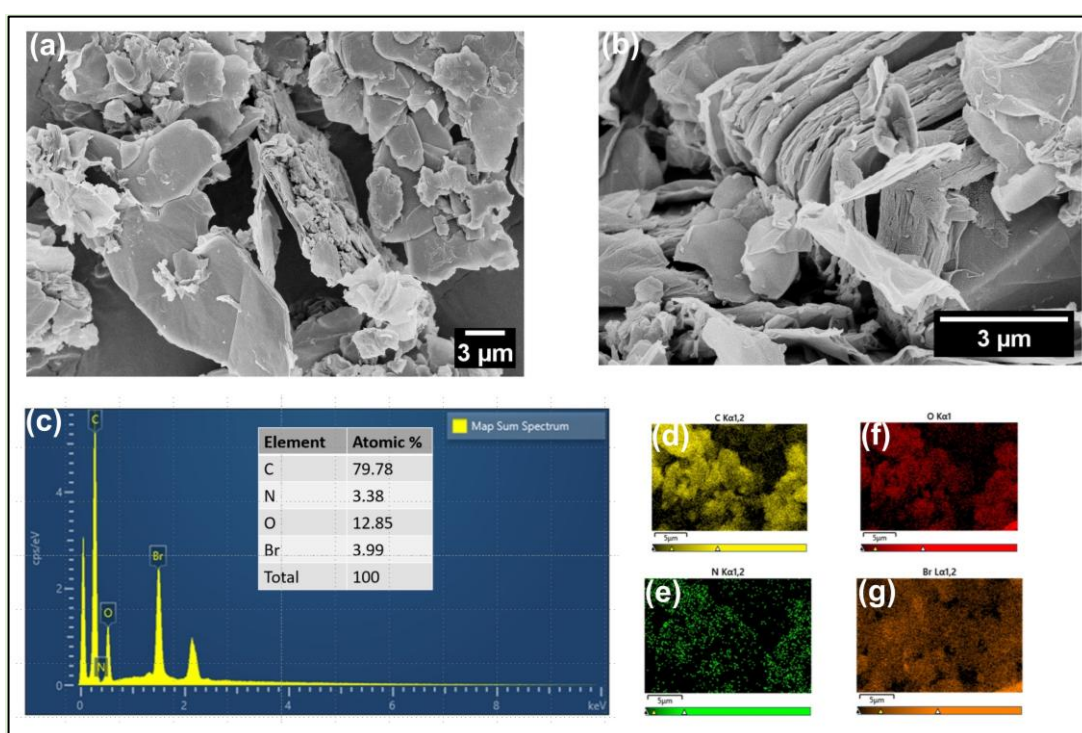


Figure 6.5. (a, b) FESEM images of DFG. (c) EDS elemental mapping illustrating the elemental distribution in DFG. Elemental distribution maps for (d) Carbon, (e) Nitrogen (f) Oxygen and (g) Bromine.

Elemental composition and distribution were further examined using energy-dispersive X-ray (EDX) spectroscopy. Quantitative EDX analysis shows atomic percentages of C, N, O, and Br to be 79.78%, 3.38%, 12.85%, and 3.99%, respectively, which is in good agreement with the elemental composition trends obtained from XPS measurements (Figure 6.5 (c)). Elemental mapping (Figure 6.5 (d)–(g)) confirms a homogeneous spatial distribution of bromine and nitrogen across the graphene sheets,

suggesting that functionalization occurs not only at the sheet edges but also at defect sites and within the basal planes of graphene [40].

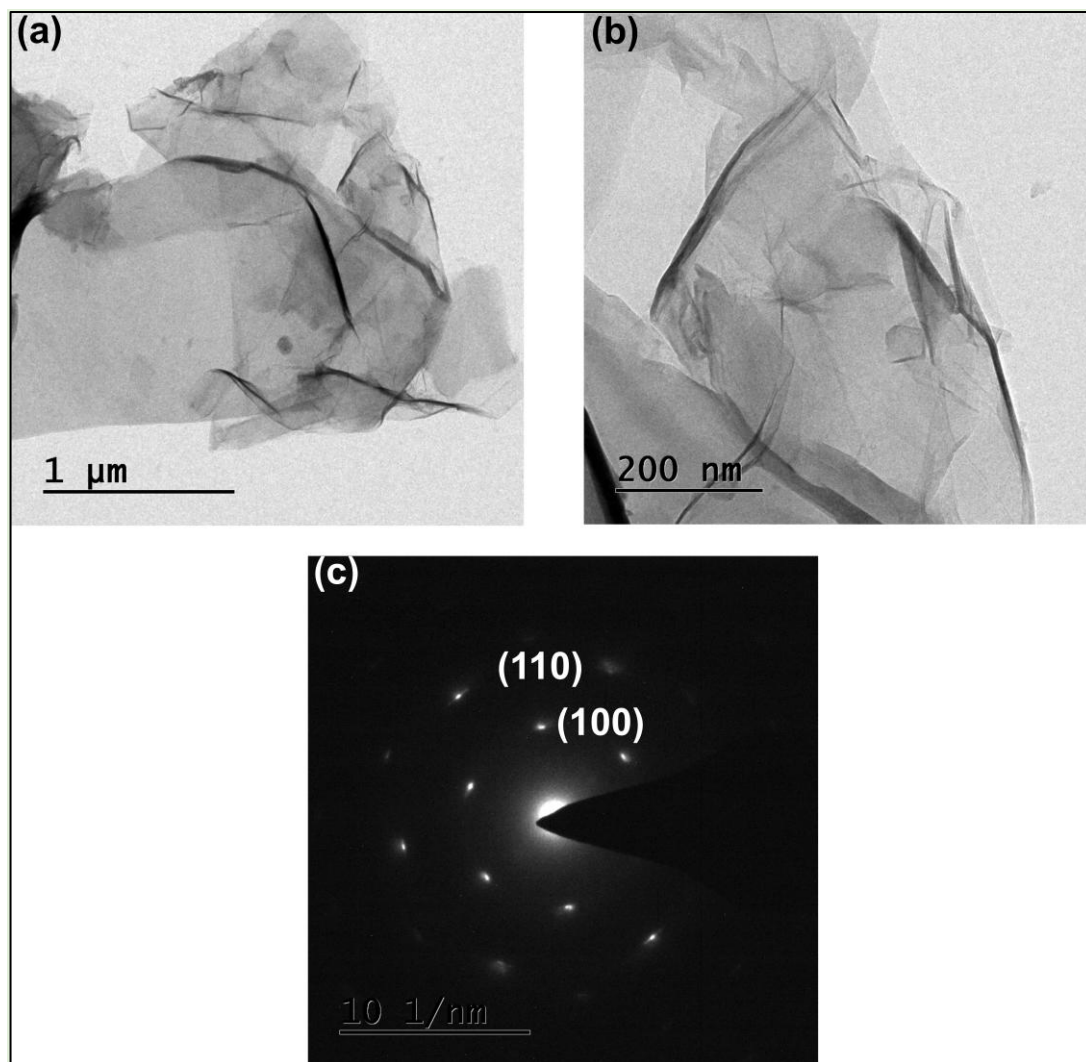


Figure 6.6. (a, b) HRTEM images of DFG. (c) Corresponding SAED pattern of DFG.

HR-TEM analysis provides further insight into the nanoscale structure of DFG (Figure 6.6 (a)–(b)). The TEM images reveal regions with varying contrast, where highly transparent areas correspond to few-layer graphene, whereas darker regions arise from wrinkling, folding, and localized stacking of sheets. Importantly, no rips, tears, or nanoscale holes are observed, indicating that the graphene framework remains structurally intact at the nanoscale. Nevertheless, DFG shows a tendency for scrolling, wrinkling, and folding of initially flat graphene sheets, leading to the formation of

localized few-layer and multilayer regions [21]. The crystalline nature of DFG was further confirmed by selected area electron diffraction (SAED, Figure 6.6 (c)).

The SAED patterns exhibit distinct diffraction spots arranged in a six-fold symmetry, characteristic of the hexagonal graphitic lattice, confirming that the fundamental crystalline structure of graphene is retained after functionalization [21]. The observed concentric diffraction rings exhibit interplanar spacings of approximately 0.207 nm and 0.120 nm, which can be indexed to the {100} and {110} planes of graphene, respectively [45]. The presence of ring-like diffraction patterns rather than isolated sharp spots indicates that DFG consists of multiple randomly oriented graphene domains, reflecting its polycrystalline nature. Such diffraction behaviour is analogous to that observed in powder X-ray diffraction patterns of graphene-based materials [21,45].

6.3.2 Electrochemical performance of the SSCs

To evaluate the energy-storage performance of the as-prepared DFG, symmetric supercapacitors were fabricated in a CR2032 coin-cell configuration using 4.09 M EMIMBF₄/ACN as the electrolyte (Figure 6.7 (a)). The electrochemical performance was systematically investigated through cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge–discharge (GCD) measurements. For comparison and to quantify the enhancement arising from dual functionalization, a control symmetric supercapacitor was also assembled using RG (before functionalization) as the electrode material. For clarity, the devices are hereafter referred to as DFG SC and RG SC, respectively.

The stable operating potential window (OPW) of the device was first determined by recording CV curves of the representative DFG SC at a scan rate of 10 mV s^{−1} over a voltage range of 2.6–3.4 V (Figure 6.7 (b)). The corresponding coulombic efficiency (CE) values for different voltage windows are presented in Figure 6.7 (c). Analysis of the data reveals that the CE remains nearly constant (~100%) from 2.6 to 3.1 V and retains a high value of 96.1% at 3.2 V. However, upon further expansion of the voltage

window, a sharp decrease in CE is observed, reaching 86.88 % for 3.4 V which can be attributed to the onset of parasitic redox reactions.

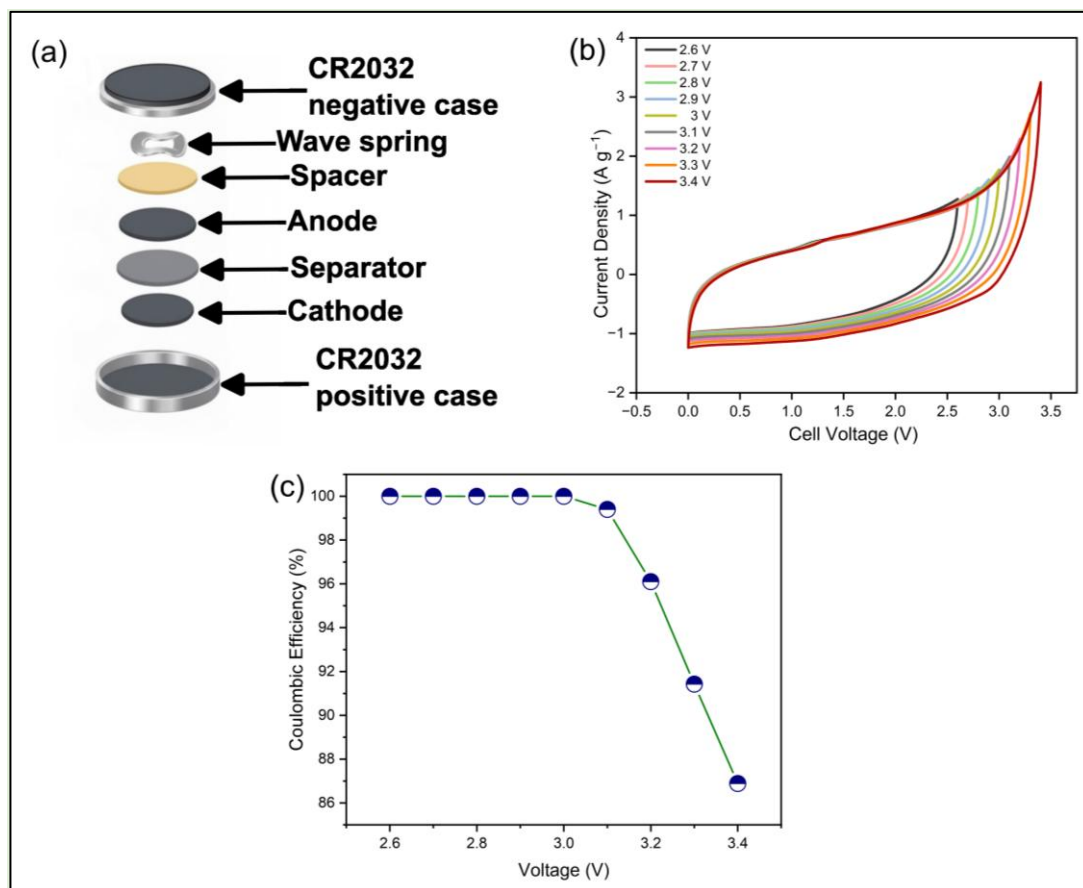


Figure 6.7. (a) Schematic representation of the CR2032-type coin-cell assembly. (b) Cyclic voltammetry (CV) curves of the DFG-based supercapacitor recorded at a scan rate of 10 mV s^{-1} at different operating voltage windows (2.6–3.4 V). (c) Corresponding coulombic efficiency values.

Consistent trends are also evident from the shape of the CV profiles. When the voltage window is extended from 2.6 to 3.2 V, the CV curves maintain a quasi-rectangular shape, indicative of capacitive behavior. In contrast, widening the potential window to 3.3 V results in a sudden increase in current, leading to the appearance of a small hump in the CV curve.

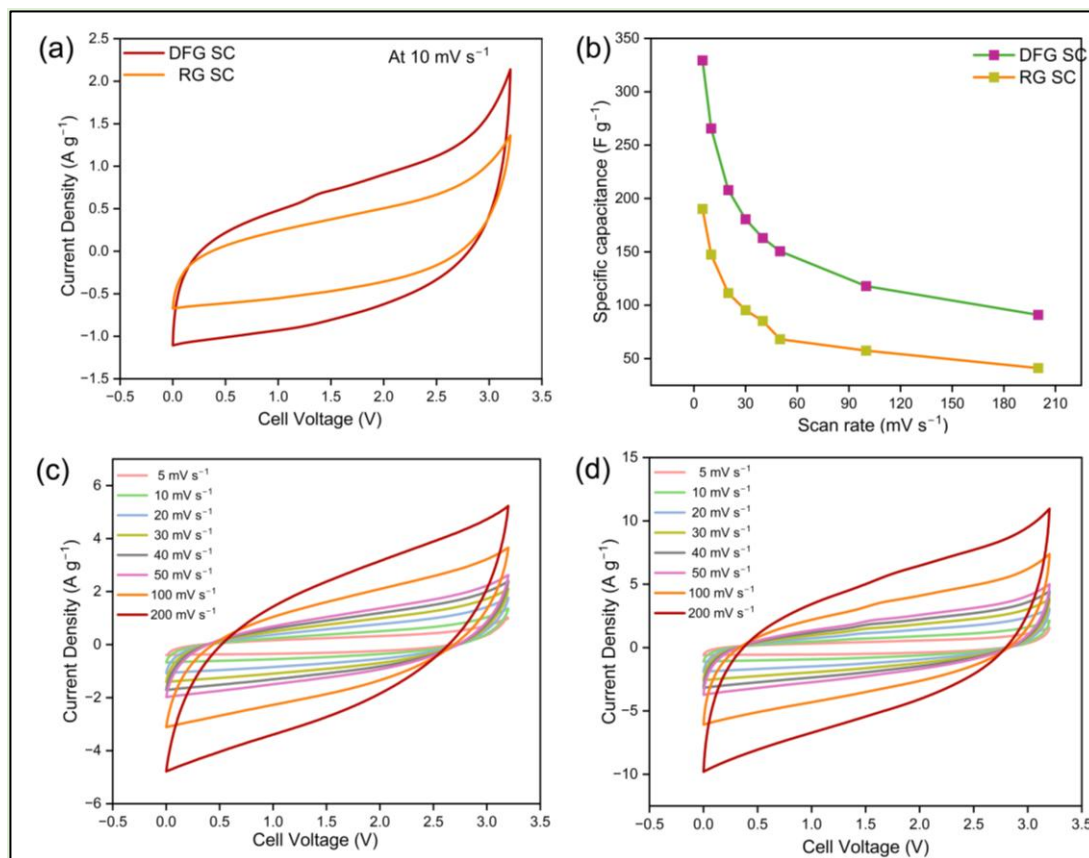


Figure 6.8. (a) CV curves of RG SC and DFG SC recorded at a scan rate of 10 mV s⁻¹. (b) Variation of specific capacitance with scan rate. (c) CV curves of RG SC measured at different scan rates. (d) CV curves of DFG SC measured at different scan rates.

These features become more pronounced at higher voltages, suggesting electrolyte decomposition or side reactions. Based on these observations, an operating potential window of 3.2 V was selected as the optimal and stable operating window for all subsequent electrochemical studies. Notably, this finding is in good agreement with previously reported results [46], where a similar operating potential window of 3.2 V was achieved using a 4.09 M EMIMBF₄ electrolyte and activated carbon electrodes. Therefore, it can be reasonably concluded that 3.2 V represents a safe and stable operating potential window for the fabricated devices. The long-term stability of the DFG SC is further confirmed through cycling tests over 10,000 charge–discharge cycles at a current density of 10 A g⁻¹, as discussed in the subsequent sections.

The CV curves of the DFG SC and RG SC recorded at a scan rate of 10 mV s^{-1} are presented in Figure 6.8 (a). As evident from the figure, the DFG SC encloses a significantly larger CV area than the RG SC, indicating a pronounced enhancement in electrochemical performance. To quantitatively assess this improvement, the specific capacitance values were calculated from the CV curves of both devices, and the results are summarized in Figure 6.8 (b). The DFG SC delivers a high specific capacitance of $\sim 180 \text{ F g}^{-1}$, in stark contrast to $\sim 50 \text{ F g}^{-1}$ for the RG SC, corresponding to an enhancement of approximately 200%.

This substantial improvement is particularly noteworthy, as it is achieved solely through surface functionalization of RG, without incorporating additional components to form composites or heterostructures. Thus, modulation of surface chemistry alone provides a remarkable boost in charge-storage capability. Furthermore, the DFG SC retains $\sim 57.42\%$ of its initial capacitance upon a ten-fold increase in scan rate (150.57 F g^{-1} at 50 mV s^{-1}), whereas the RG SC retains only $\sim 25.45\%$, demonstrating the superior rate capability of DFG.

The CV curves of both DFG SC and RG SC recorded at various scan rates ranging from 5 to 200 mV s^{-1} are shown in Figures 6.8 (c) and (d) respectively. A closer inspection of these Figures reveals that the CV profiles of both RG SC and DFG SC exhibit a quasi-rectangular shape rather than the ideal rectangular shape typically associated with pure electric double-layer capacitors. Additionally, very weak redox features are discernible, particularly at lower scan rates, suggesting that the overall capacitance arises from a combined contribution of electric double-layer capacitance and pseudocapacitance. In view of this mixed charge-storage behavior, it becomes necessary to evaluate the b -value, which provides insight into the dominant charge-storage mechanism governing the device performance.

According to the power-law relationship, the dependence of peak current (i) on the scan rate (ν) can be expressed as:

$$i = a\nu^b \quad (6.7)$$

Or,

$$\log i = \log a + b \log v \quad (6.8)$$

Where, a and b are adjustable parameters. The b -value provides insight into the dominant charge-storage mechanism. A b -value of 0.5 indicates that the current response scales with the square root of the scan rate ($i \propto v^{1/2}$), characteristic of diffusion-controlled processes. On the other hand, a b -value of 1 suggests a linear dependence of current on scan rate ($i \propto v$), corresponding to a surface-controlled capacitive behaviour and values between 0.5 and 1, imply mixed charge-storage contributions arising from both capacitive and diffusion-limited processes.

To determine the b -values, plots of $\log(i)$ versus $\log(v)$ were constructed for the anodic and cathodic peaks (insets of Figure 6.9 (a)–(b)). The extracted b -values for both devices are summarized in Figure 6.9 (a)–(b). In the present study, RG SC and DFG SC exhibit b -value of ~ 0.60 and ~ 0.64 , indicating that their charge-storage behavior is predominantly governed by ion-diffusion-controlled processes. This trend aligns well with previous reports on functionalized graphene systems, where the transformation of local sp^2 domains into sp^3 configurations, defect generation, and surface-chemistry modulation are known to (i) increase the number of electrochemically accessible active sites, (ii) enhance electrolyte wettability and ion accessibility, and (iii) suppress sheet restacking, which collectively leads to improved electrochemical performance [7,47].

Further, the charge-storage mechanism was quantitatively evaluated using Dunn's method by separating the total CV current into capacitive and diffusion-controlled components at different scan rates. At a given potential (V), the current response is expressed as

$$i(V) = k_1 v + k_2 v^{1/2} \quad (6.9)$$

Where, k_1v and $k_2v^{1/2}$ represent capacitive and diffusion-controlled contributions, respectively.

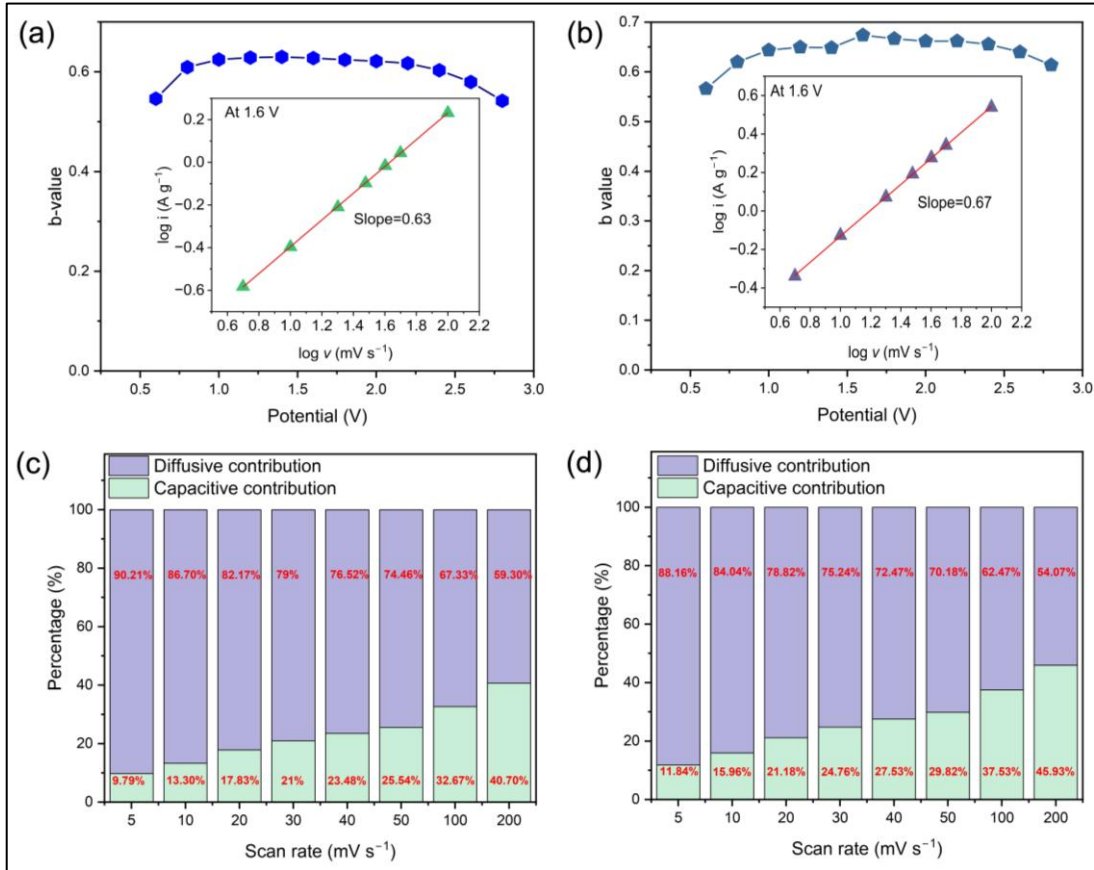


Figure 6.9. Variation of the b-value as a function of applied potential for (a) RG SC and (b) DFG SC, with insets showing representative log(i) versus log(v) plots. Relative capacitive and diffusion-controlled charge storage contributions at different scan rates for (c) RG SC and (d) DFG SC.

Rearranging Equation (6.9) gives

$$\frac{i(V)}{v^{1/2}} = k_1 v^{1/2} + k_2 \quad (6.10)$$

The parameters k_1 and k_2 were obtained from the slope and intercept of plots of $\frac{i(V)}{v^{1/2}}$ versus $v^{1/2}$ constructed using CV data at multiple scan rates. Substitution of these values into Equation (6.9) enabled quantitative determination of capacitive and diffusion-controlled contributions at each potential.

The relative capacitive and diffusion-controlled contributions at different scan rates are summarized in Figures 6.9 (c–d). At low scan rates, the charge-storage process is predominantly governed by diffusion-controlled mechanisms because electrolyte ions have sufficient time to penetrate into the bulk of the electrode material. As the scan rate increases, the capacitive contribution gradually increases owing to the limited time available for ion diffusion, thereby promoting surface-controlled charge-storage processes. For the RG SC, the capacitive contribution increases from 9.79% at 5 mV s⁻¹ to 40.70% at 200 mV s⁻¹. Correspondingly, the diffusion-controlled contribution decreases from 90.21% to 59.30%, indicating that diffusion processes remain the dominant charge-storage mechanism across the investigated scan-rate range. Similarly, the DFG SC device exhibits capacitive contributions of 11.84% at 5 mV s⁻¹, which increase further to 45.93% at 200 mV s⁻¹. Despite this increase, the diffusion-controlled process still dominates, contributing 54.07% at 200 mV s⁻¹.

Thus, both devices exhibit diffusion-dominated charge storage, although the DFG SC displays relatively higher capacitive contributions compared to RG SC, particularly at higher scan rates. This behaviour suggests that functionalization enhances surface-controlled electrochemical processes while maintaining significant diffusion-controlled ion transport within the electrode.

Figure 6.10 (a) presents the GCD profiles of the DFG SC and RG SC recorded at a current density of 1 A g⁻¹, while Figure 6.10 (b)–(c) shows the corresponding GCD curves obtained over a wide range of current densities from 1 to 20 A g⁻¹. The nearly symmetric charge–discharge profiles with slight curvature and Coulombic efficiencies approaching 100% indicate capacitive behaviour and excellent electrochemical reversibility [8]. Notably, the DFG SC exhibits a longer charge–discharge duration than the RG SC at the same current density, reflecting its superior energy-storage performance. At 1 A g⁻¹, the DFG SC delivers a high specific capacitance of 171.25 F g⁻¹, significantly exceeding that of the RG SC (73.12 F g⁻¹), corresponding to an enhancement of over 134%. This improvement demonstrates the effectiveness of amine and bromine functionalization in enhancing charge-storage capability. Figure 6.10 (d) summarizes the variation of specific capacitance with current density in the

range of 1–20 A g^{-1} . Even at a high current density of 20 A g^{-1} , DFG SC retains a specific capacitance of 38.63 F g^{-1} , which is substantially higher than that of the RG SC (11.12 F g^{-1}), representing an improvement of approximately 247%. This excellent rate capability highlights the suitability of the DFG SC for high-power and demanding energy-storage applications.

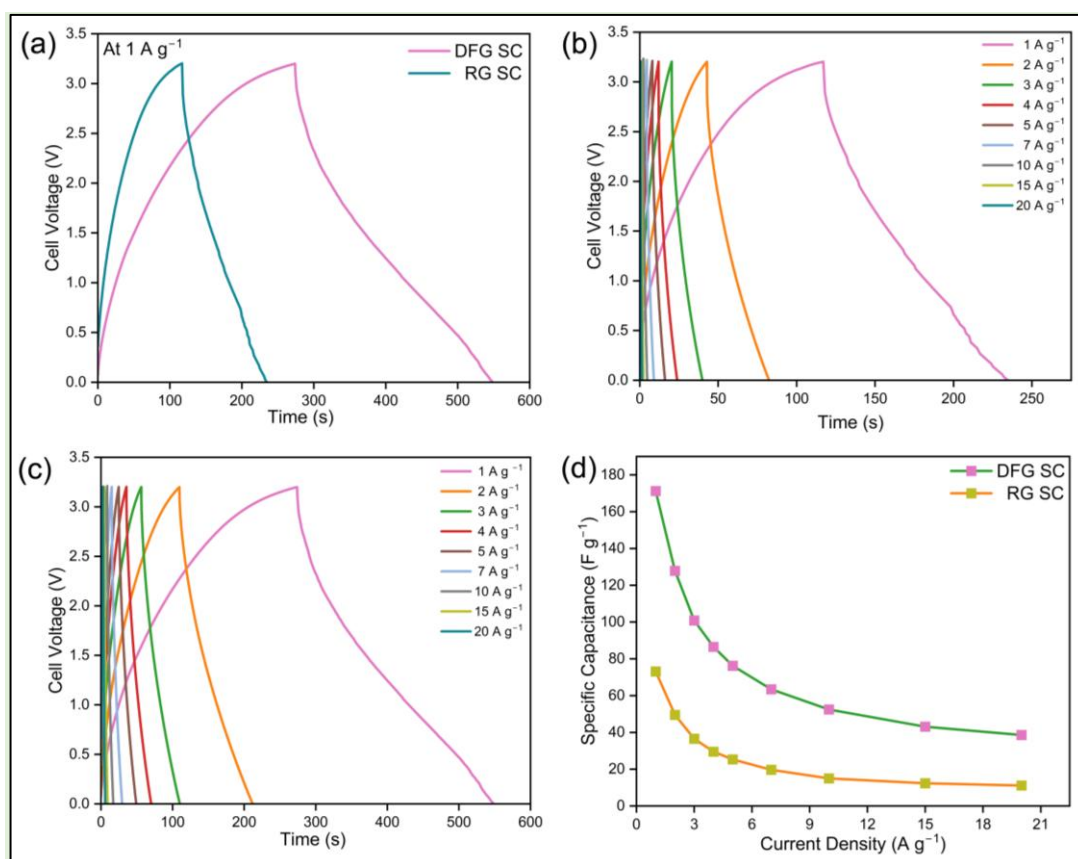


Figure 6.10. (a) GCD curves of RG SC and DFG SC at a current density of 1 A g^{-1} . (b) GCD curves of RG SC at various current densities. (c) GCD curves of DFG SC at various current densities. (d) Specific capacitance of RG SC and DFG SC as a function of current density.

Additionally, the DFG SC demonstrated impressive performance, delivering both high energy and power densities. Compared with the RG SC, an improvement of over 149.6 % in energy density is observed at the same power density. Specifically, the DFG SC achieves an energy density of 60.89 Wh kg^{-1} at a power density of 800 W kg^{-1} , whereas the RG SC delivers only 26 Wh kg^{-1} under identical conditions. Notably,

even at a high-power density of $16,000 \text{ W kg}^{-1}$, the DFG SC maintains a remarkable energy density of 13.73 Wh kg^{-1} .

These results are summarized in Table 6.4 and it can be seen that the energy–power characteristics of the DFG SC surpass those of previously reported ionic- and organic-electrolyte-based supercapacitors and even outperforms devices based on emerging two-dimensional layered materials. The superior combination of high energy and power densities highlights the strong potential of the DFG-based graphene supercapacitor for next-generation energy-storage applications, including electric vehicles.

Table 6.4: Reported electrochemical performance of representative supercapacitor devices.

Sl. No.	Materials	Electrolyte	Voltage window (V)	Energy density (Wh kg^{-1})	Power density (W kg^{-1})	Ref
1	Activated carbon	BMPY-TFSI	3	25	100	[48]
2	ReS ₂	TEABF ₄	2	28.5	500	[49]
3	Porous graphene macroform	1 M TEABF ₄ /ACN	2.5	23.5	63	[50]
4	MoS ₂ nanosheets	0.5 M TEABF ₄	3	20.68	--	[51]
5	Graphene/V ₂ O ₅	LiClO ₄ /PC	2.5	80.4	275	[52]
6	MoSe ₂ nanosheets	0.5 M TEABF ₄	3	20.31	1125	[53]
7	Porous carbon	EMIMBF ₄	2	20	3100	[54]
8	Siloxene	0.5 M TEABF ₄	3	5.08	375	[55]

9	Poly(ionic liquid)-modified rGO	[MPPy] [TFSI]	2	40	2100	[56]
10	Blue Sheets	TiO ₂ 1M TEABF ₄	3	6	750	[57]
11	BDA/rGO	1M TEABF ₄ /ACN	2.5	34	425	[58]
12	Defective boron nanosheet	BMIMBF ₄	3	25.1	636.1	[59]
13	Tris-rGO	TEABF ₄	3.5	51	552	[60]
14	Silicon oxycarbide	TEABF ₄	3	20.89	750	[61]
15	Graphene-CMK-5	EMIMBF ₄	3.5	60.7	174	[62]
16	Reduced graphene oxide	BMIPF ₆	4	18.9	2800	[63]
17	Reduced graphene oxide	[SET ₃][TFSI]	2.5	17.7	875	[64]
18	Hydrothermally prepared rGO	TEABF ₄	3	35.58	7500	[65]
19	Sonochemically prepared rGO	TEABF ₄	3	38.07	1500	[66]
20	Graphene	TEABF ₄	3	44.95	750	[67]
21	DFG SC	4.09 M EMIMBF ₄	3.2	60.89	800	This work
22	RG SC	4.09 M EMIMBF ₄	3.2	26	800	

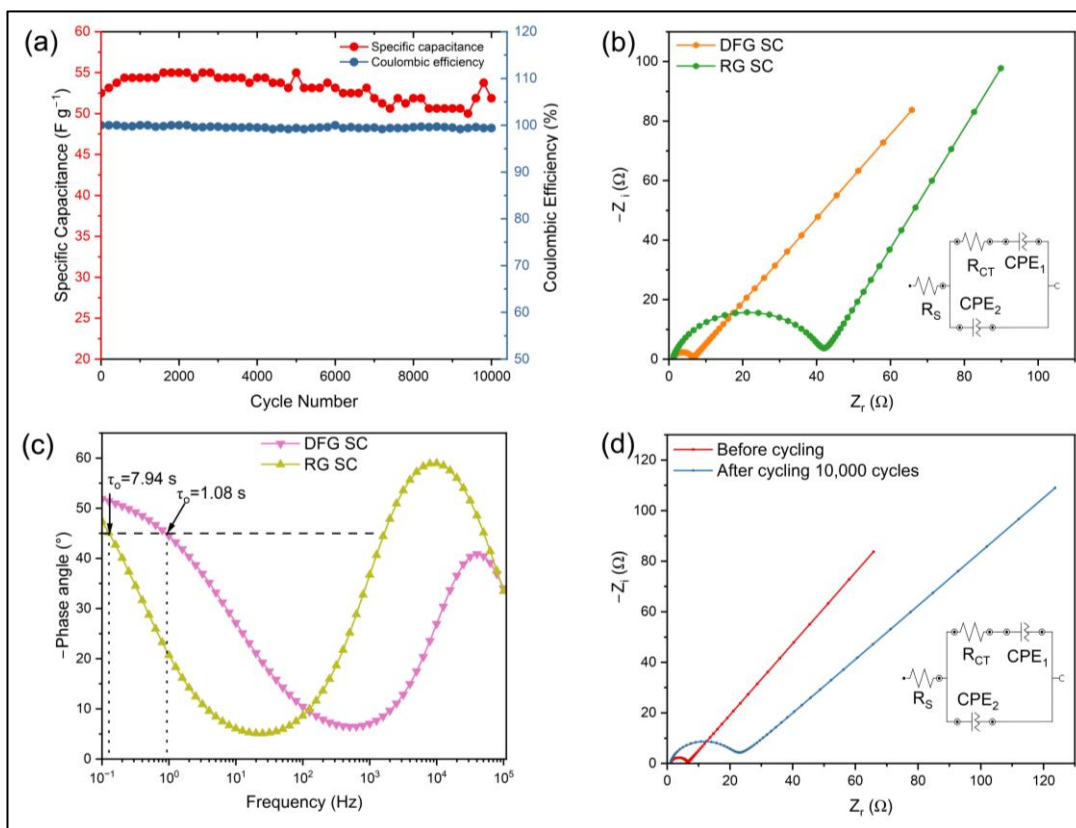


Figure 6.11. (a) Cycling stability of RG SC and DFG SC measured at 10 A g^{-1} over 10,000 cycles. (b) Nyquist plots of RG SC and DFG SC with the inset displaying the equivalent circuit employed for fitting the EIS spectra. (c) Bode plots of RG SC and DFG SC with the corresponding relaxation times. (d) Nyquist plots of DFG SC before and after cycling, with the inset showing the equivalent circuit used for fitting the EIS spectra.

Furthermore, cycling stability, which is a key requirement for the long-term operation of supercapacitor devices, is further examined for the DFG SC. The device shows negligible degradation, retaining 98.41% of its initial capacitance after 10,000 charge–discharge cycles at 10 A g^{-1} (Figure 6.11 (a)), indicating excellent durability. The electrochemical processes were further examined using electrochemical impedance spectroscopy (EIS). Figure 6.11 (b) shows the Nyquist plots of the DFG SC and RG SC, while the corresponding Bode plots are presented in Figure 6.11 (c). To ensure reliable fitting, multiple models were evaluated, and the optimal circuit was selected based on the lowest χ^2 value (Table 6.5). The equivalent circuit that provides the best

agreement with the experimental data is shown as an inset in Figure 6.11 (b) and (d), with the extracted circuit parameters and associated fitting errors summarized in Table 6.5.

Table 6.5: Circuit element values and fitting errors for the equivalent circuit model (inset of Figure 6.11 (b) and (d)) obtained from EIS data at OCP.

Device	Circuit Element		Value	Estimated Error (%)	χ^2
RG SC	R_s		1.001	3.315	0.07
	R_{CT}		40.737	0.997	
	CPE ₁	Y_0	1.629×10^{-5}	6.677	
		n	0.8379	0.751	
	CPE ₂	Y_0	0.0127	1.820	
		n	0.7077	1.580	
DFG SC (Before cycling)	R_s		0.9852	4.201	0.04
	R_{CT}		5.3999	1.426	
	CPE ₁	Y_0	6.41×10^{-5}	15.394	
		n	0.8996	1.525	
	CPE ₂	Y_0	0.0130	0.952	
		n	0.6070	0.626	
BG-20 SC (After cycling for 10,000 cycles @ 20 A g ⁻¹)	R_s		0.9714	1.256	0.07
	R_{CT}		20.607	1.377	
	CPE ₁	Y_0	1.073×10^{-5}	7.239	
		n	0.8747	0.720	
	CPE ₂	Y_0	0.0085	1.296	
		n	0.5202	1.215	

As evident from Figure 6.11 (b), the DFG SC exhibits lower solution resistance (R_s) and charge-transfer resistance (R_{CT}) compared to the RG SC. This reduction in resistive components is likely associated with the presence of amine and bromine

functional groups, which enhance electrolyte wettability and facilitate improved ion transport and interfacial charge transfer, as reported in previous studies [7]. Further, the Bode phase plots of both devices are shown in Figure 6.11 (c). The frequency at which the phase angle reaches -45° , known as the knee frequency (f_0), represents the transition point where resistive and capacitive contributions are equal and is commonly used to estimate the relaxation time ($\tau_0 = 1/f_0$) of supercapacitor systems. A shorter relaxation time reflects faster electrochemical kinetics and superior rate capability. The knee frequencies of the DFG SC and RG SC are determined to be 0.93 Hz and 0.13 Hz, corresponding to relaxation times of 1.08 s and 7.94 s, respectively, confirming the faster charge–discharge response of the DFG SC.

To further assess long-term stability, EIS measurements were repeated for the DFG SC after 10,000 charge–discharge cycles, as shown in Figure 6.11 (d), with the pre-cycling spectrum identical to that presented in Figure 6.11 (b). The post-cycling impedance data were fitted using the same equivalent circuit model, and the extracted parameters are listed in Table 6.5. After cycling, the R_s remained almost same, while the R_{CT} increases by about 15.20 Ω . This slight rise in R_{CT} can be attributed to minor aging effects of the electrode material, such as increased surface roughness or interfacial irregularities at the electrode–electrolyte interface. Importantly, the overall impedance response remains largely unchanged, underscoring the excellent electrochemical stability of the DFG SC during prolonged cycling.

6.3.3 Temperature-dependent performance of the DFG SC for application in EVs

To assess the practical suitability of the DFG SC for electric vehicle (EV) applications, stable electrochemical performance over a wide temperature range is essential. Accordingly, the temperature-dependent electrochemical behaviour of the DFG SC is systematically investigated from -15°C to 100°C . Figure 6.12 illustrates the electrochemical performance of the DFG SC across a broad temperature range. Figure 6.12 (a) shows the cyclic voltammetry (CV) profiles recorded at a scan rate of 100 mV s^{-1} , which retain a quasi-rectangular shape at all investigated temperatures, indicating preserved capacitive behaviour. Typically, a reduction in temperature leads to a

noticeable decrease in the enclosed CV area due to hindered ion transport, while higher temperatures generally enhance capacitance. In contrast, the CV areas of the DFG SC vary only marginally with temperature, suggesting remarkably stable charge-storage behaviour across the entire range. At 20 °C, the specific capacitance is obtained from CV curves is 117.96 F g⁻¹, and even at -15 °C it remains at 102.27 F g⁻¹ (Figure 6.12 (b)). Similarly, the specific capacitance remains nearly constant between 40 and 100 °C, indicating minimal thermal sensitivity.

This trend is further corroborated by GCD measurements recorded at a current density of 5 A g⁻¹ (Figure 6.12 (c)). The specific capacitances computed from the GCD curves (Figure 6.12 (d)) closely follow the behaviour observed in the CV analysis. Compared to the value at 20 °C, the capacitance at -15 °C shows only a slight decrease of approximately 22%, while increasing the temperature does not lead to any significant enhancement or deterioration in capacitance. Specifically, the capacitance values at 40°C, 60°C, 80°C, and 100 °C remain comparable at ~70 Fg⁻¹ to that obtained at room temperature, underscoring the excellent thermal robustness of the device. Such stability is highly desirable for real-world applications, where energy-storage systems are required to operate under widely varying environmental conditions.

The minimal variation in capacitance with temperature can be rationalized using EIS, with Nyquist plots at different temperatures shown in Figure 6.12 (e). As the temperature decreases to -15 °C, both the solution resistance (R_s) and charge-transfer resistance (R_{CT}) increase, reflecting reduced ionic conductivity and slower interfacial kinetics. At 20 °C, R_s and R_{CT} are ~0.98 Ω and ~5.40 Ω , respectively, while at -15 °C, R_{CT} increase to 22.50 Ω . This pronounced rise in R_{CT} at low temperature likely accounts for the modest reduction in specific capacitance observed under sub-zero conditions.

With increasing temperature, the solution resistance decreases to 0.63, 0.64, 0.56, and 0.55 Ω at 40 °C, 60 °C, 80 °C, and 100 °C, respectively, indicating improved ionic transport. However, the charge-transfer resistance simultaneously increases to 10.02, 13.11, 14.86, and 14.89 Ω over the same temperature range. This compensating effect

between reduced R_S and increased R_{CT} likely results in the nearly constant capacitance observed at elevated temperatures.

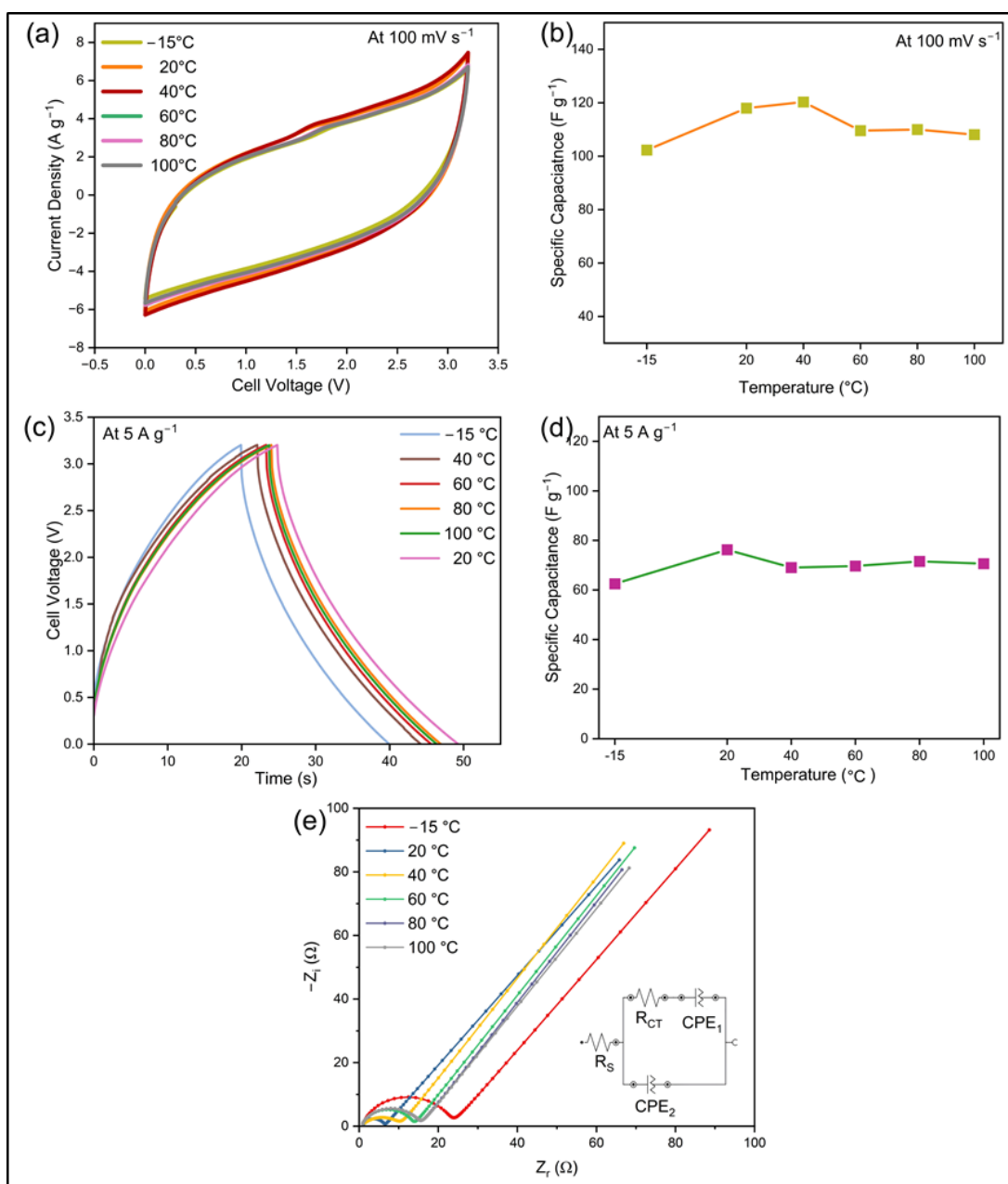


Figure 6.12. (a) CV curves of DFG SC measured over a temperature range of -15 to 100 °C. (b) Specific capacitance calculated from the CV data. (c) GCD curves of DFG SC at 5 A g⁻¹ under different temperature conditions. (d) Specific capacitance obtained from the GCD measurements at various temperatures. (e) Nyquist plots of DFG SC recorded at different temperatures.

Overall, these findings demonstrate that the DFG SC maintains stable electrochemical performance over a broad temperature range, highlighting its strong potential as a reliable energy-storage device for EV and other demanding applications.

6.3.4 Performance of DFG SC for capturing RRBE in EVs

Further experiments were conducted to evaluate, at a proof-of-concept level, the suitability of the high-performance DFG supercapacitor (SC) as a potential auxiliary electrical energy storage unit for regenerative braking energy capture in electric vehicles (EVs). In modern EV architectures, lithium-ion batteries typically function as the primary energy source, delivering sustained energy for propulsion (Figure 6.13 (a)). However, batteries are inherently limited in their ability to accommodate the sudden, high-power current pulses generated during braking events. Consequently, supercapacitors are increasingly explored as complementary energy-storage devices that operate in conjunction with batteries to buffer transient power spikes, thereby mitigating battery degradation, reducing thermal stress, and extending overall battery lifetime. Owing to their intrinsically high-power density, rapid charge–discharge capability, excellent cycling stability, and near-maintenance-free operation, supercapacitors are particularly attractive for regenerative braking systems, where fast energy capture and delivery are essential.

In this context, a simple laboratory-scale regenerative braking prototype was employed to qualitatively demonstrate the suitability of the developed DFG SC for capturing braking-induced electrical energy. It is emphasized that a comprehensive evaluation of regenerative braking efficiency and vehicle-scale energy recovery lies beyond the scope of the present work. Rather, the objective of this experiment is to provide a proof-of-concept demonstration indicating that the developed DFG SC, owing to its excellent electrochemical characteristics, is capable of accepting and storing transient electrical energy generated during braking events. Therefore, a laboratory-scale regenerative braking prototype, conceptually similar to that previously reported by Kim and co-workers [3,4], was employed in the present study. The prototype was assembled using DC mini electric motors and electrical components procured from commercial sources.

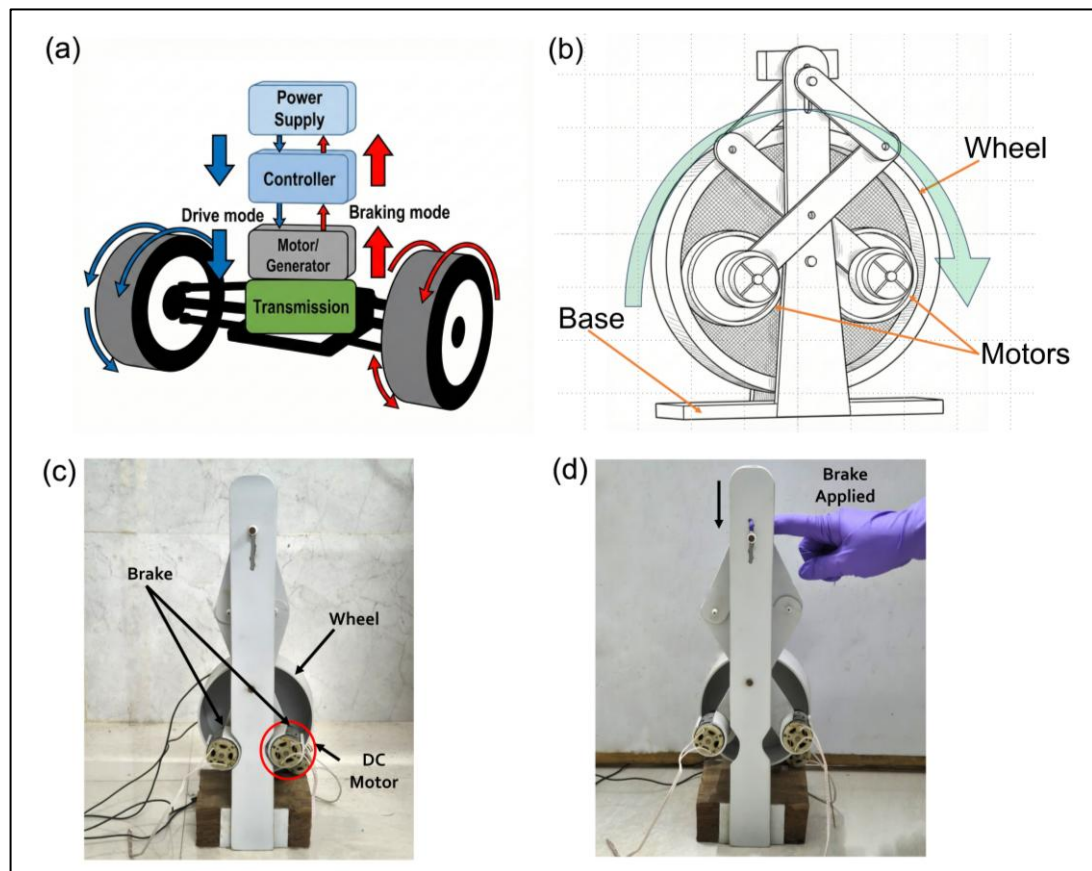


Figure 6. 13. (a) Working principle of the regenerative braking energy process in electric vehicles (EVs). (b) Schematic representation of the regenerative braking system employed. (c) Digital photograph of the prototype used for RRBE studies during the driving mode, and (d) during the braking mode.

During braking, the motor operates as a generator, where the kinetic energy associated with the motion of the rotating system, which would otherwise be dissipated as heat through friction, is partially converted into electrical energy. The generated electrical energy is subsequently directed toward an external energy-storage unit, where it can be temporarily stored and made available for reuse.

Such regenerative energy capture strategies are widely recognized for their potential to improve overall energy efficiency, reduce net energy consumption, and lower associated CO₂ emissions in electric vehicle systems [3]. In this context, the DFG SC developed in the present work is particularly attractive, as it delivers a high-power density of approximately 16,000 W kg⁻¹ along with an impressive energy density of

13.73 Wh kg⁻¹, well aligned with the power requirements typically proposed for auxiliary energy-storage components in next-generation electric vehicles. A schematic illustration of the experimental configuration is shown in Figure 6.13 (b), while the laboratory-scale model constructed in this work is presented in Figure 6.13 (c)-(d). The system consists of a flywheel assembly that represents the kinetic energy of a vehicle in motion, mechanically coupled to DC motors and equipped with a friction-based braking mechanism. An external DC power source is used exclusively to accelerate the flywheel to a desired rotational speed prior to the braking experiment. Importantly, this external power source is electrically disconnected during the regenerative braking measurements to ensure that the observed electrical response originates solely from the deceleration process.

The ability of the DFG SC to accept electrical energy generated during braking was evaluated by monitoring its open-circuit voltage response under manually controlled braking conditions. Upon application of mechanical braking, the rotational kinetic energy in the flywheel drives the coupled DC motor into an electromechanical energy-generation regime, leading to the development of back electromotive force during deceleration. The resulting voltage response at the terminals of the DFG SC was recorded as a function of time for different braking intensities, and the corresponding voltage–time profiles are presented in Figure 6.14 (a).

When the system operates in acceleration or steady-rotation mode, with no braking force applied, the voltage of the DFG SC remains essentially unchanged, indicating the absence of charging. In contrast, the application of mechanical braking produces distinct voltage transients, with the magnitude of the voltage response increasing systematically with braking intensity. Under mild braking conditions, the terminal voltage of the DFG supercapacitor increases to approximately 0.76 V, whereas a rapid braking pulse results in a voltage rise of up to 2.08 V (Figure 6.14 (b)). These observations clearly indicate the generation of electrical voltage driven by the deceleration process during braking. The obtained results are consistent with the results obtained by Kim and co-workers, where they observed a similar trend when

they utilised a graphene supercapacitor and 2D siloxane-graphene heterostructure for capturing regenerative braking [3,4].

While the above measurements confirm the generation of electrical voltage during braking, voltage transients alone do not necessarily imply net energy storage. To further examine whether the generated electrical energy can be effectively captured and retained within the supercapacitor, a Schottky diode (1N5819, 1A 40V) was introduced between the motor output and the positive terminal of the DFG SC. The Schottky diode serves as an electrical isolation element, ensuring unidirectional current flow from the motor to the supercapacitor while preventing reverse discharge of stored energy back into the motor during non-braking periods. This modification enforces a controlled energy-flow pathway and enables clearer distinction between transient voltage generation and actual energy storage.

The corresponding voltage–time response recorded in the presence of the diode is shown in Figure 6.14 (c). In the absence of braking, no voltage rise is observed, whereas upon application of mechanical braking, a sustained increase in the supercapacitor voltage is recorded, indicating net energy capture within the device. These observations demonstrate that, although supercapacitors are capable of absorbing very high-power inputs, the extent of regenerative energy recovery in practical systems is strongly influenced by the associated power-electronic elements, which may act as limiting factors.

Finally, to demonstrate practical energy delivery capability, two DFG SCs connected in series were employed to power an array of 25 red light-emitting diodes (LEDs) with a forward operating voltage of 1.65–2.0 V and a rated current of 20 mA. Following charging, the stored energy was sufficient to continuously illuminate the LEDs for more than 12 minutes (Figure 6.14 (d)–(g)), highlighting the ability of the assembled device to deliver stable electrical power over extended durations. This demonstration further underscores the potential of the developed DFG supercapacitor for real-world energy-storage applications involving intermittent, high-power energy capture.

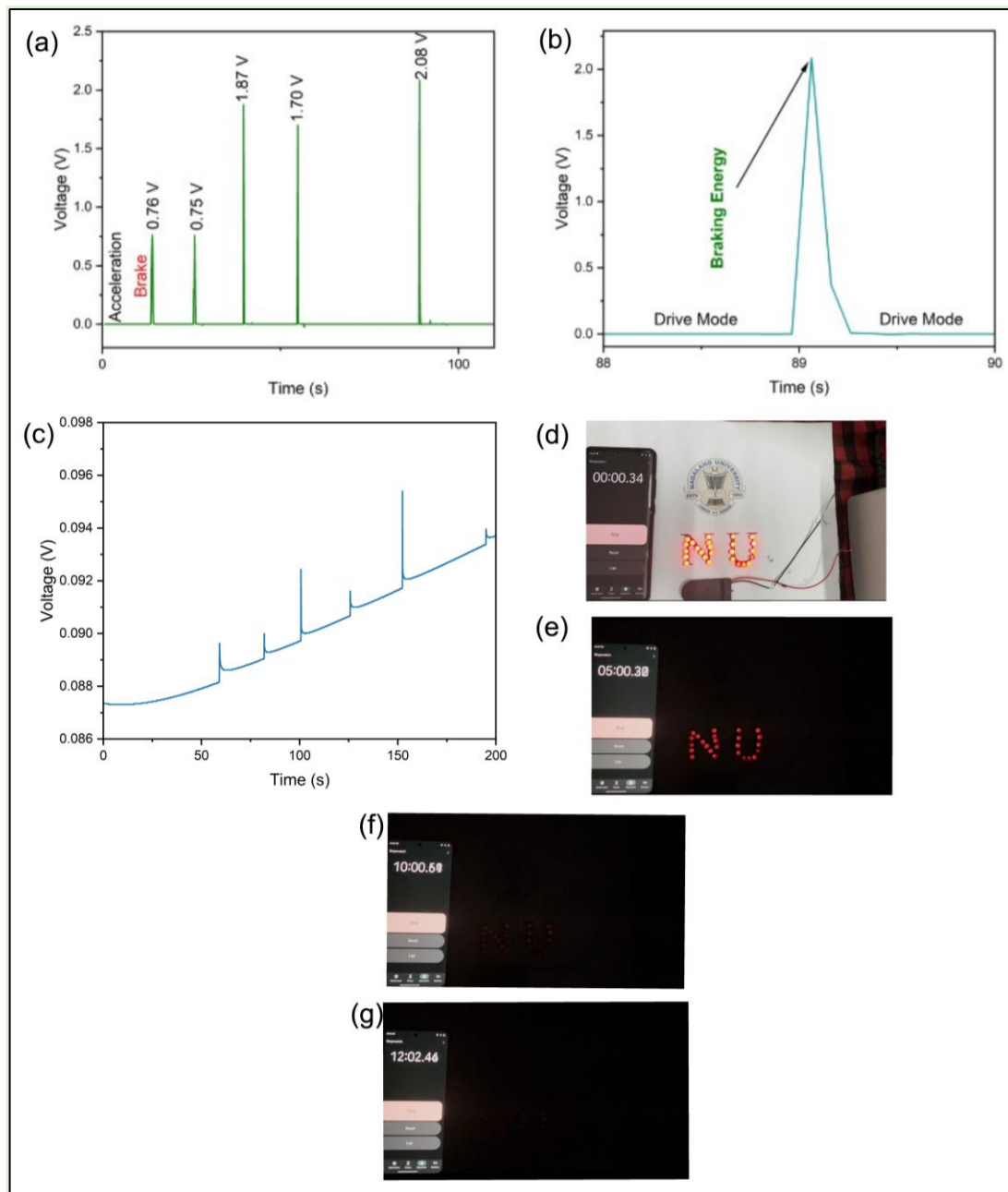


Figure 6.14. (a) Voltage versus time response of the DFG SC during driving and braking modes. (b) Magnified section, highlighting the voltage rise to 2.08 V, confirming the applicability of DFG SC for regenerative braking energy storage in EVs. (c) Voltage–time response of the DFG SC during driving and braking with a Schottky diode, demonstrating charge retention after braking. (d–g) Photographs showing two DFG SCs connected in series powering 25 LEDs after 0, 5, 10, and 12 min, respectively.

6.4 Conclusion

This work demonstrates a rapid and effective strategy for the simultaneous incorporation of bromine and nitrogen functionalities onto the RG's surface. XPS analysis reveals a bromine content of ~9.38 at.%, with Br 3d deconvolution indicating that ~97.02% of the bromine is covalently bonded, while only ~2.98% exists as physisorbed Br⁻ species. Deconvolution of the N 1s spectrum confirms that amine groups are the predominant nitrogen species after functionalization. Elemental mapping shows a uniform distribution of bromine and nitrogen across the DFG's surface, while Raman spectroscopy indicates that vacancy-type defects dominate the defect structure.

When employed as a supercapacitor electrode, DFG SC exhibits a remarkable enhancement in electrochemical performance. Specifically, surface functionalization of RG to DFG results in a 134% increase in specific capacitance, while at a power density of 800 W kg⁻¹, a 149.6% improvement in energy density is achieved. In addition, the DFG SC demonstrates excellent cycling stability, retaining its performance with only a marginal loss of 1.19% after 10,000 charge–discharge cycles at a current density of 10 A g⁻¹. Temperature-dependent electrochemical studies further indicate that the DFG-based supercapacitor operates reliably over a wide temperature range from -15 °C to 100 °C, maintaining nearly constant performance. The simultaneous introduction of bromine and nitrogen functionalities leads to reduced solution resistance and charge-transfer resistance compared to RG. Finally, as a proof of concept, the practical applicability of the DFG-based supercapacitor was demonstrated by integrating it with a regenerative braking system for, highlighting its capability to store electrical energy generated during braking. The excellent energy–power characteristics, wide operating temperature window, and demonstrated real-world applicability establish DFG as a promising high-performance energy storage material with potential for regenerative braking energy capture in next-generation electric vehicles.

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Chapter 7

NH₂-functionalized reduced graphene oxide as a high-performance adsorbent for naphthalene: A combined experimental and DFT study

CHAPTER 7

NH₂-functionalized reduced graphene oxide as a high-performance adsorbent for naphthalene: a combined experimental and DFT study

7.1 Introduction

One of the newly identified pollutants that have gained more focus are polycyclic aromatic hydrocarbons (PAHs). PAHs are organic compounds made up of two or more fused aromatic rings [1]. This category of pollutants has drawn considerable public attention because of its possible threat to both the environment, human health and regular detection in environmental samples such as surface water, soil, and edibles [2]. PAHs make their way into the environment via multiple pathways, such as incomplete combustion of fuels, mining of coal, engine oil leakages, degradation of organic matter by biological agents, and petroleum refining processes [2–5]. Consequently, they are exacerbating the ongoing issue of contaminating the water environment, resulting in global warming and further damage to ecosystems. PAH release has been especially important in urbanized and industrialized countries. Although present in relatively small amounts, environmental levels of these PAHs have been progressively rising in recent years [1,3]. Further, the stability of benzene rings renders PAHs insensitive to natural degradation processes and hence results in their continued accumulation in the environment [6]. PAHs display numerous adverse health effects in humans, even though these are variable according to the individual PAH in question [7–9]. Nonetheless, the greatest reason for concern about PAHs is their carcinogenic potential [10,11]. As a result, the United States Environmental Protection Agency (US EPA) has identified 16 such PAHs (Figure 7.1) as emerging pollutants, such as naphthalene (NAP) [12].

The most dominant constituent among PAHs is NAP [4], known for its hydrophobic nature, flammability, great volatility, and chemical stability in water mediums [13]. NAP is present in moth repellents, cigarettes, and deodorants [14] and is utilized in industries to synthesize phthalic anhydride, methyl anthranilate and compounds such as surfactants and pigments [15]. The US EPA allowed limit of NAP is 0.6 mg L⁻¹ [16]. High concentrations of NAP in water can lead to severe health problems, including hemolytic anaemia in children [17]. The harmful effects of NAP on health and its universal occurrence in the environment have made it necessary to develop efficient ways to purify polluted water bodies.

In this context, different technologies such as biodegradation, membrane separation, phytoremediation, photo-oxidation, chemical oxidation, coagulation and electrochemical degradation have been investigated [2,18–23].

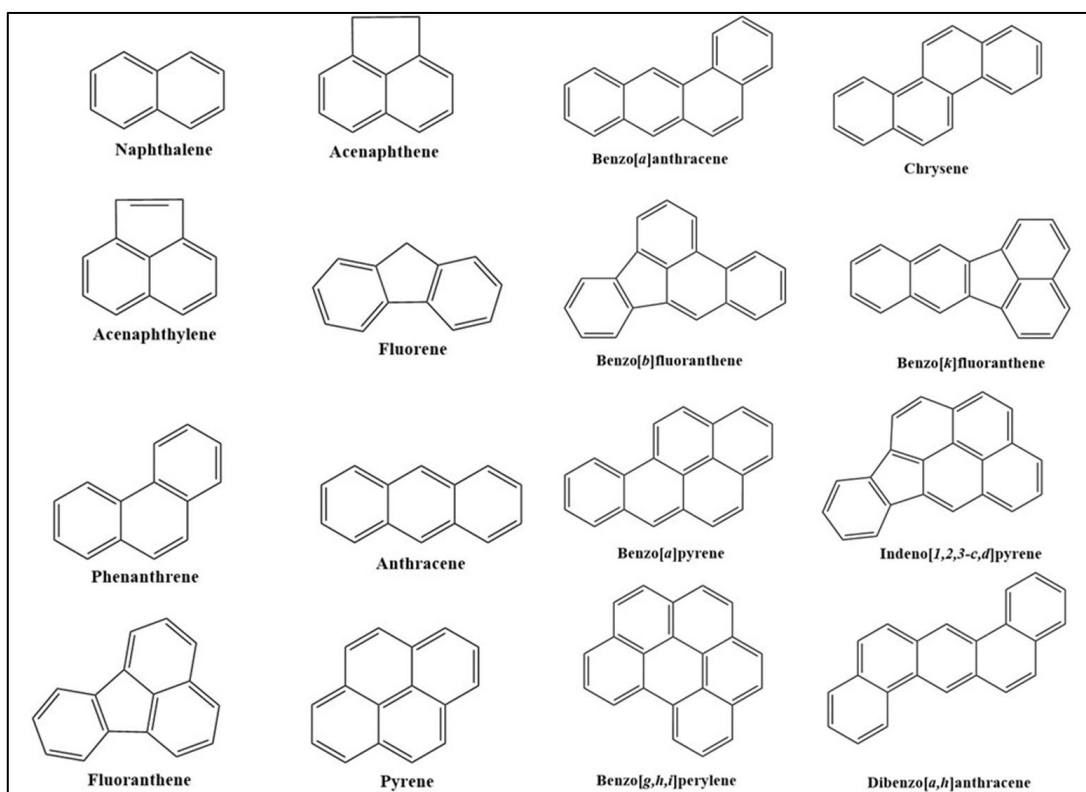


Figure 7.1. Chemical structures of the 16 PAH compounds designated as U.S. EPA priority pollutants.

Most of these, though, are associated with difficulties like high equipment costs, generation of toxic by-products, complicated equipment setup etc. Among the methods available, adsorption remains most widely accepted treatment technique for removing many organic and inorganic pollutants from wastewater due to its ease of use, cost-effectiveness, ease of operation and excellent capability to remove effectively a wide range of pollutants [24].

In the adsorption process, the adsorbent plays a crucial role in determining how effectively a pollutant is removed. Therefore, it is imperative to develop novel adsorbents that can eliminate a wide range of contaminants from water. Carbon-based materials such as graphene have emerged as one of the most promising materials in

the field of adsorption [25–27]. Further, the ability to fine-tune graphene's properties by introducing heteroatoms such as nitrogen, sulphur, phosphorus or functionalising graphene with different functional groups makes it appealing for use in numerous fields [28,29]. Several reports have shown that modifying graphene-based adsorbents with specific functional groups can significantly enhance the adsorption capacity [30–32]. For instance, Elhamid et al. [33] reported that citrate-modified graphene oxide significantly improved methylene blue, crystal violet and inorganic copper and cobalt uptake. In another study, lignosulfonate-modified graphene hydrogel demonstrated ultrahigh adsorption capacity for Pb^{2+} [34]. As a result, a major focus of current research is the surface modification of graphene-based materials for the selective adsorption of targeted pollutants. Recently, aminated graphene (NH_2 group bonded to graphene framework) has attracted considerable interest due to its potential for diverse applications, including adsorbents in adsorption [29]. Presently, there exist various methodologies for the synthesis of aminated graphene [35–37]. Nevertheless, these reports require high temperatures, are time-consuming, consist of many steps, involve further processing, and hence unsuitable for large-scale production [29]. Moreover, instead of formation of amines, high temperatures lead to the incorporation of nitrogen-containing heterocycles, including pyridines, pyrroles, quaternary or pyridinic-N-oxides [36].

Further, the surface functional groups of graphene play a pivotal role in governing adsorption behavior. A quantitative insight into how different functionalities make their respective contributions to adsorption can thus guide the rational design and optimization of more effective adsorbent materials for the removal of pollutant. Quantification of such effects using conventional experimental techniques is however, frequently troublesome owing to surface interaction complexity. In this context, Density Functional Theory (DFT) serves as a powerful computational tool, offering valuable insights into the surface chemistry involved in naphthalene adsorption, thereby enabling the rational design of more effective adsorbent materials.

To the best of the authors' knowledge, no earlier reports on the application of aminated reduced graphene oxide for the removal of polycyclic aromatic hydrocarbons (PAHs)

have been reported. Therefore, the primary objective of this study is to investigate the potential of aminated reduced graphene oxide for naphthalene (NAP) removal. Furthermore, there is a notable gap in understanding the relationship between the functional groups of the adsorbent and the adsorptive capacities for NAP in aqueous solutions. Consequently, this study also aims to examine the influence of the various functional groups and their role in NAP removal, utilising DFT for a deeper molecular-level analysis. Additionally, while this study demonstrates the use of aminated graphene for NAP removal, its application can be extended to other PAHs as well.

7.2 Materials and methods

7.2.1 Materials

Graphite powder (< 20 μm , Sigma-Aldrich), sulfuric acid (98%, Sigma-Aldrich), potassium permanganate (Sigma-Aldrich), ethanol (Sigma-Aldrich), ammonia solution (Sisco Research Laboratories Pvt. Ltd., India), de-ionized water (Resistivity 18.2 M Ω cm @ 25°C), and L-ascorbic acid (Sisco Research Laboratories Pvt. Ltd., India) were utilized in the synthesis of aminated graphene. All chemicals were of analytical grade and were used as received without further purification.

7.2.2 Synthesis of aminated graphene and reduced graphene oxide

Aminated graphenes with varying amine contents were synthesised following the procedure outlined in our previous work [29]. Briefly, 23 mL of concentrated sulfuric acid (H_2SO_4) was introduced to 1 g of graphite powder, and the mixture was cooled with an ice bath to mitigate any temperature rise. Potassium permanganate (KMnO_4 , 6 g) was then slowly added in small portions to the reaction mixture while ensuring that the temperature did not exceed 10 °C, with continuous stirring. Afterwards, the ice bath was removed, and the reaction mixture was stirred at 35 °C for 30 minutes, followed by the addition of 70 mL of de-ionised water (DI H_2O). The reaction mixture was then subjected to sonication for 30 minutes and stirred for an additional 30 minutes. Subsequently, the solution's pH was then adjusted precisely using ammonia to four specific values of 5, 7, 9, and 12, yielding four corresponding samples labelled Am-rGO@5, Am-rGO@7, Am-rGO@9, and Am-rGO@12. After reaching the

desired pH, 100 mL of a 1 M L-ascorbic acid solution was added. The reaction mixture was then refluxed at 95 °C for one hour. Following this, the mixture was centrifuged at 6,000 rpm for 10 minutes at room temperature and washed with DI H₂O until the pH reached ~7. The resulting blackish powder was dried in a vacuum oven at 60 °C overnight to yield aminated graphene. For comparative purposes, reduced graphene oxide (rGO) was prepared using the same procedure, with NaOH substituted for ammonia to achieve a pH of 7.

A comprehensive description of characterisation of the prepared samples can be found in our previous work [29]. In particular, the elemental compositions of the aminated graphene samples, as determined by XPS analysis, are summarized in Table 7.1.

Table 7.1: Atomic concentrations of C, N, and O in aminated graphene samples obtained from XPS analysis.

Sample	% Carbon	% Nitrogen	% Oxygen
Am-rGO@5	78	2.48	19.3
Am-rGO@7	76.3	5.95	17.5
Am-rGO@9	76	2.98	20.7
Am-rGO@12	82.7	1.93	15.2

Thus, the degree of amination follows the order:

Am-rGO@7 > Am-rGO@9 > Am-rGO@5 > Am-rGO@12

Further, to ascertain whether the nitrogen species were covalently bonded to the graphene framework or merely physisorbed on its surface, high-resolution C 1s and N 1s spectra were recorded and deconvoluted (Figure 7.2). As shown in Figure 7.2 (a–d), the peak observed at 285.8 eV in all samples corresponds to C–N bonding, confirming successful amination. Additionally, deconvolution of the N 1s spectra (Figure 7.2 (e–f)) reveals the presence of various nitrogen configurations depending on the synthesis conditions. Notably, all samples exhibit a component at 399.8 eV which is assigned to primary amine (–NH₂) groups.

The relative concentrations of nitrogen functionalities obtained from N 1s deconvolution are summarized in Table 7.2. Among the samples, Am-rGO@7 exhibits the highest primary amine content (81.32%), followed by Am-rGO@9 (60.28%), Am-rGO@12 (39.31%), and Am-rGO@5 (35.93%).

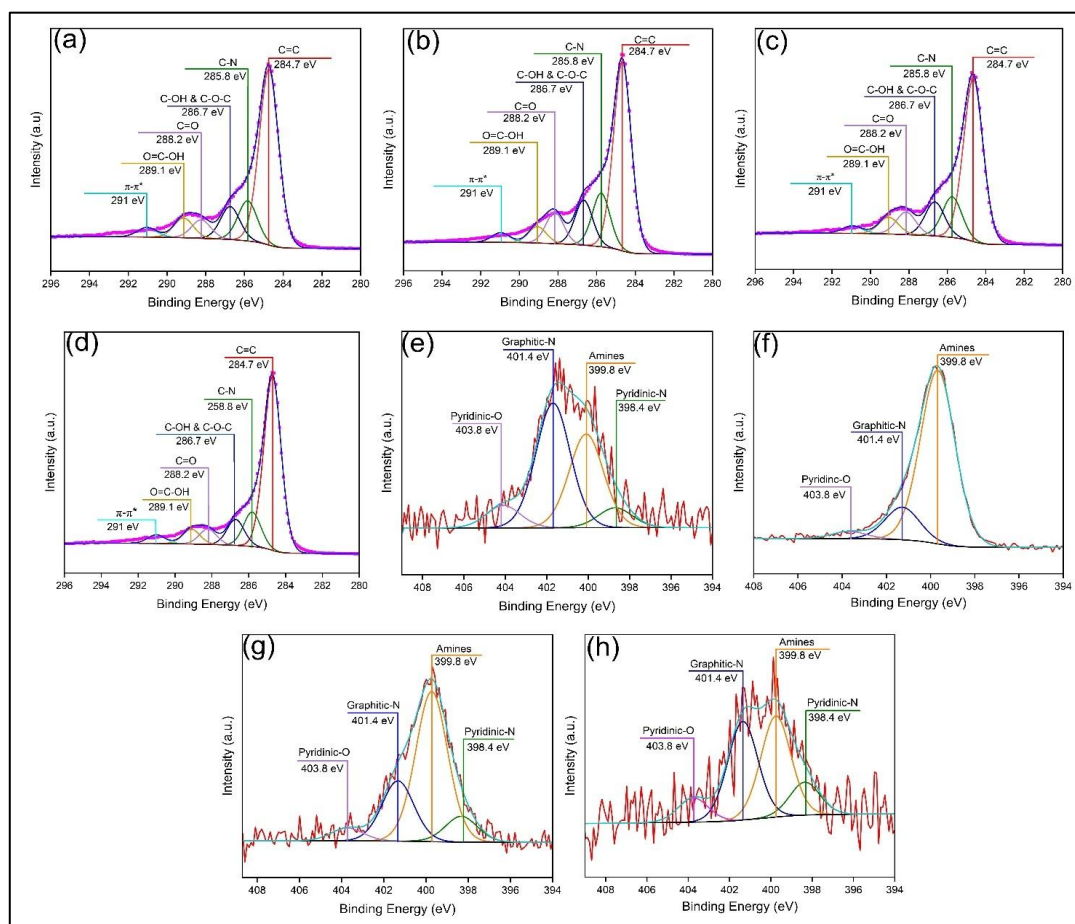


Figure 7.2. Deconvoluted HR-XPS spectra of C1s region of (a) Am-rGO@5 (b) Am-rGO@7 (c) Am-rGO@9 and (d) Am-rGO@12. Deconvoluted HR-XPS spectra of N 1s region of (e) Am-rGO@5 (f) Am-rGO@7 (g) Am-rGO@9 and (h) Am-rGO@12. Reproduced with permission from [29].

Table 7.2: Relative concentrations (%) of nitrogen containing functional groups obtained from deconvoluted HR-XPS spectra of N1s of all samples.

Component	Pyridinic-N	Primary Amines	Graphitic-N	Pyridinic-O
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Binding Energy (eV)	398.4	399.8	401.4	403.8
Am-rGO@5	7.60	35.93	47.85	8.61
Am-rGO@7	--	81.32	15.28	3.40
Am-rGO@9	10.36	60.28	24.19	5.18
Am-rGO@12	12.82	39.31	38.39	9.48

7.2.3 Adsorption studies

The removal of NAP onto aminated graphenes was conducted using a batch adsorption method. In this method, 50 mL of a 30 mg L⁻¹ NAP solution was added to a 100 mL Erlenmeyer flask, followed by the addition of a measured amount of adsorbent. The mixture was stirred on a rotary shaker at 200 rpm until adsorption equilibrium was achieved. Aliquots of the sample were collected at regular intervals, filtered through Whatman Grade-1 filter paper, and then the absorbance was measured at 275.6 nm using a UV-visible spectrophotometer (Shimadzu, UV-2600 i) equipped with a quartz cuvette of 1.0 cm path length. Triplicate measurements were performed for all experiments.

Due to the limited solubility of NAP in water, an ethanol–water mixture was used as the solvent. To prepare the stock solution, 30 mg of naphthalene was dissolved in 50 mL of ethanol and then diluted with 950 mL of deionised water, resulting in a final concentration of 30 mg L⁻¹. The solution was stored at room temperature in sealed glass containers, protected from light.

The removal efficiency (%) and the NAP adsorption capacity (mg/g) were calculated using Equations 7.1 and 7.2, respectively.

$$\text{Removal efficiency (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (7.1)$$

$$q_e = \frac{(C_i - C_e)V}{W} \quad (7.2)$$

where, C_i (mg L^{-1}) = initial NAP concentration; C_e (mg L^{-1}) = NAP concentration at equilibrium; $W(\text{g})$ = amount of adsorbent; V (L) = Volume of solution used in batch experiment; q_e = NAP adsorption capacity. All batch experiments were conducted at room temperature (24 ± 2 °C), unless otherwise specified.

7.2.4 Computational details

Computational methodology

All quantum calculations were performed with the Gaussian 16W software package [38], employing the B3PW91 functional in combination with the 6-31G(d,p) basis set [39–50]. The B3PW91 functional, which combines Becke's three-parameter exchange functional and the PW91 correlation functional, has been shown to provide accurate results for large systems of molecules [49–51]. Geometry optimisations were carried out to get the lowest energy conformations, followed by frequency calculations, all conducted without imposing any symmetry constraints. The lack of imaginary frequencies assured that the optimised structures were indeed true minima on the potential energy surface. To account for solvation effects, the polarizable continuum model using the integral equation formalism variant (IEFPCM) was employed, which enables the estimation of total free energy in solution by incorporating both electrostatic and non-electrostatic contributions [52]. Further, to accurately account for long-range van der Waals (vdW) interactions, which are critical in describing physisorption and significantly influence adsorption energy calculations, empirical dispersion corrections were incorporated using Grimme's DFT-D3 method [53,54].

The adsorption energy (E_{ad}) of NAP on the adsorbents was calculated as follows [55]:

$$E_{ad} = E_{(adsorbent+NAP)} - (E_{NAP} + E_{adsorbent}) \quad (7.3)$$

where, $E_{adsorbent+NAP}$, E_{NAP} and $E_{adsorbent}$ represents the energy of the adsorbent+NAP system, NAP and the adsorbent, respectively. A more negative value of E_{ad} indicates stronger adsorption. Typically, adsorption energies less than -30 kJ/mol are indicative of physisorption, whereas values exceeding -50 kJ/mol suggest chemisorption [55].

Modelling of adsorption system

It is important to develop an appropriate model for the adsorbent surface to accurately investigate the interactions between NAP and graphene-based adsorbents. Quantum calculations involving graphene typically utilise either periodic boundary conditions or finite molecular models [51]. In the present work, the graphene surface was modelled using a cluster composed of thirty-six fused benzene rings, with the edge carbon atoms saturated by twenty-six hydrogen atoms to eliminate dangling bonds. The models utilised in the study are presented in Figure 7.3.

To elucidate the effect of surface chemistry on NAP adsorption, graphene was functionalized with groups commonly found on its surface, namely $-\text{COOH}$, $-\text{OH}$, and $-\text{COC}$. These groups were introduced at the same position on the graphene sheet to allow a consistent comparison of their adsorption behavior. Furthermore, to evaluate the specific contribution of amine functionalities, NH_2 groups were also introduced at defined sites on the graphene surface. The adsorption characteristics of these functionalized systems were then compared with those of pristine graphene to determine how different surface groups influence the overall adsorption performance.

For clarity, the models are designated as Gr-COOH, Gr-OH, Gr-COC, Gr-NH₂, and p-Gr, corresponding to graphene functionalized with $-\text{COOH}$, $-\text{OH}$, $-\text{COC}$, $-\text{NH}_2$ groups, and pristine (unfunctionalized) graphene, respectively. All molecular structures were constructed using the GaussView 6.0 visualisation software [56], and post-processing analyses, including the non-covalent interactions between NAP and various graphene surfaces, were further examined using reduced density gradient (RDG) analysis with the aid of Multiwfn [57,58] and VMD software [59].

7.3. Results

7.3.1 Adsorption performance

The adsorption performance of all samples towards NAP was evaluated and compared through batch adsorption experiments conducted under identical conditions. To elucidate the effect of amination on adsorption efficiency, a non-aminated counterpart, reduced graphene oxide (rGO), was also synthesized as described in Section 2.2. The

comparison with rGO enabled assessment of the extent to which amine functionalization enhances adsorption capability. Furthermore, the influence of key parameters including adsorbent dosage, pH, and contact time was systematically examined for all samples. The best adsorbent was then selected for further adsorption kinetics and isotherm studies.

Effect of adsorbent dose

Adsorbent dosage is a critical parameter in evaluating the feasibility of any potential adsorbent, as a lower dosage implies reduced material consumption and consequently lower cost. The effect of adsorbent dosage (5–100 mg) on NAP removal efficiency is illustrated in Figure 7.4 (a). As the adsorbent quantity increased from 5 mg to 10 mg, the NAP removal efficiency improved from 72.63% to 76.3% for rGO, followed by a decline with further dosage increase. A similar trend was observed for all aminated graphene samples. Notably, the adsorption efficiencies of all the aminated samples were consistently higher than that of rGO, confirming that amine functionalization enhances NAP adsorption. Moreover, the adsorption efficiency increased with nitrogen content. For instance, Am-rGO@7, possessing the highest nitrogen concentration, exhibited the highest removal efficiency (96.43%), followed by Am-rGO@9 (94.93%), Am-rGO@5 (89.9%), and Am-rGO@12 (88.13%).

The adsorption capacity (q_e), calculated using Equation 7.2 and presented in Figure 7.4 (a), shows a similar trend. The incorporation of amine groups increased the adsorption capacity from 114.45 mg g⁻¹ for rGO to 144.65 mg g⁻¹ for Am-rGO@7, achieving the maximum removal efficiency. However, a further increase in adsorbent dosage resulted in a decrease in both adsorption capacity and removal efficiency. This is likely due to aggregation or overlapping of active sites at higher concentrations. Similar observations have been reported in the literature, for instance, Guo et al. [60] reported that the adsorption of Cd (II) and Cu (II) decreased with increasing adsorbent dose of few layered magnetic graphene oxide. Based on these results, 10 mg was selected as the optimal adsorbent dosage for subsequent studies.

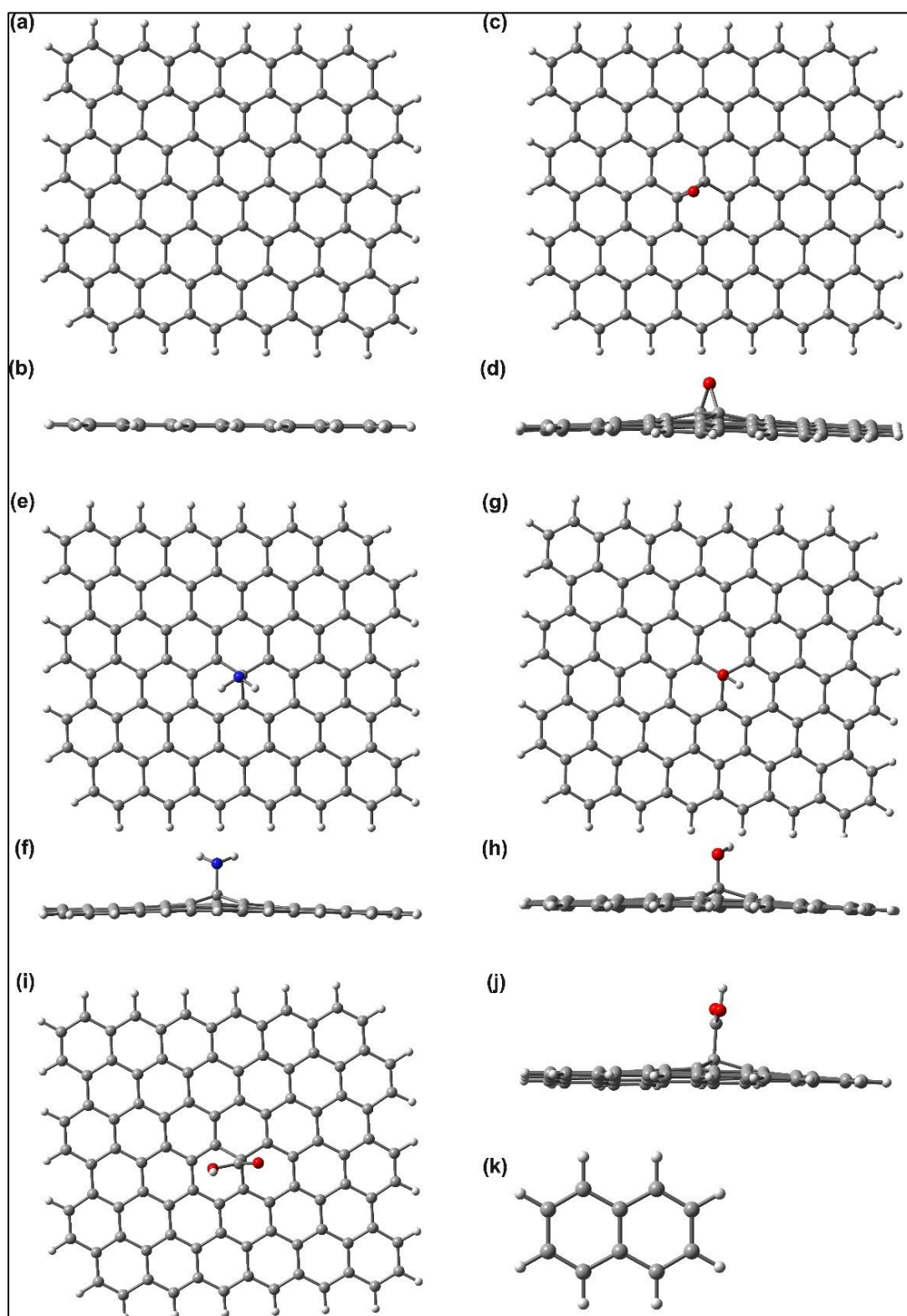


Figure 7.3. (a, b) Top and side view of p-Gr. (c, d) Top and side view of Gr-COC. (e, f) Top and side view of Gr-NH₂. (g, h) Top and side view of Gr-OH. (i, j) Top and side view of Gr-COOH. (k) NAP molecule.

Effect of pH

The adsorption of NAP is influenced by several parameters, among which solution pH plays a crucial role as it affects the surface charge of the adsorbent, the ionization state of H₂O, and the distribution of the adsorbate species [60]. Figure 7.4 (b) illustrates the effect of pH on NAP removal efficiency across a pH range of 2–10. As observed, the maximum adsorption occurred at neutral pH (pH = 7) for all tested samples. Consistent with the results obtained for adsorbent dosage, Am-rGO@7 exhibited the highest removal efficiency (96.4%), followed by Am-rGO@9 (94.7%), Am-rGO@5 (89.86%), Am-rGO@12 (88.03%), and rGO (75.96%).

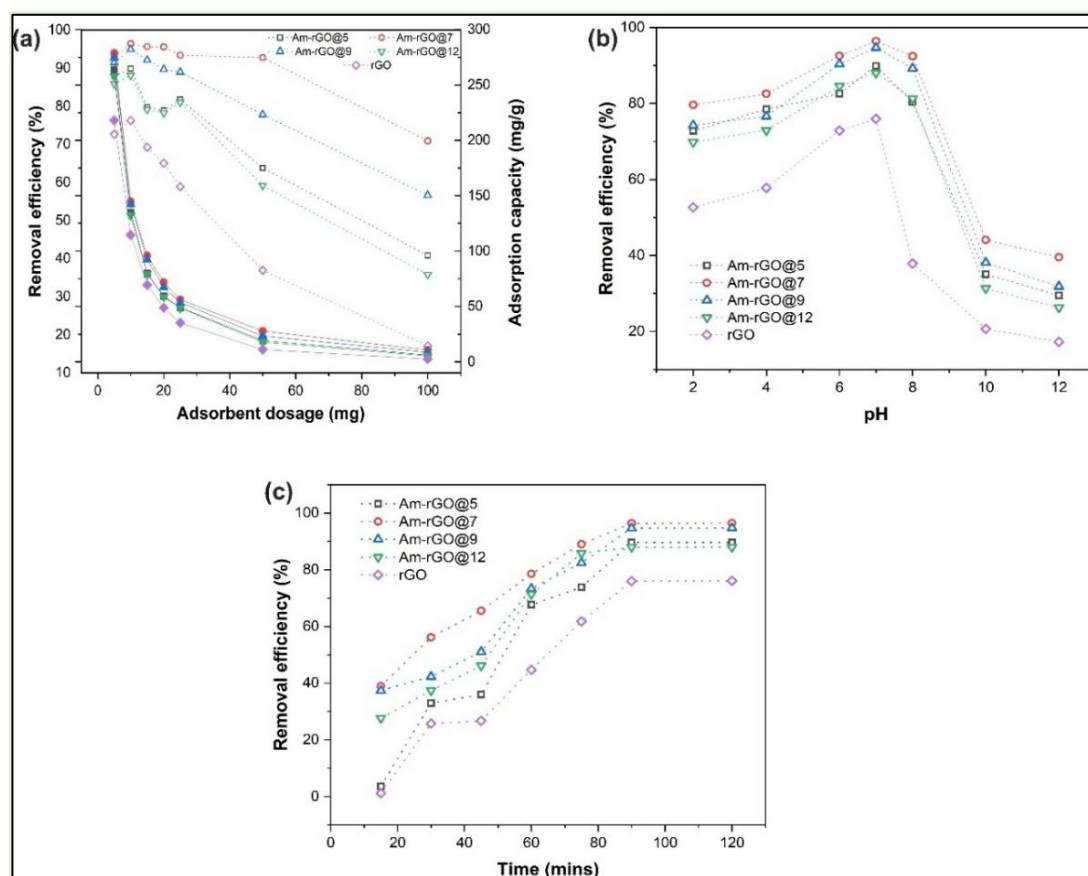


Figure 7.4. Effect of (a) adsorbent dosage, (b) pH, and (c) contact time on the adsorption of NAP onto the adsorbents.

The adsorption efficiency decreased in both acidic and basic media. In acidic medium, the functional groups commonly present in all the samples, such as $-\text{NH}_2$, $-\text{COOH}$, and $-\text{OH}$, can become protonated; thus, competition from H^+ ions and increased

surface polarity can lead to a decrease in NAP adsorption. Conversely, under alkaline conditions, the functional groups on the samples can become deprotonated, resulting in a negatively charged surface that causes electrostatic repulsion between the sheet-like structures of the samples and potentially hinders close-range π - π interactions, leading to reduced adsorption efficiency [61]. Similar results were also reported by Das et al. [62], who conducted adsorption experiments of NAP at varying pH (2–10) and found that neutral pH was optimal for NAP removal using graphene.

Effect of contact time

Contact time is one of the critical adsorption parameters, as a shorter contact time indicates higher adsorption efficiency [60]. The effect of contact time for all the samples is depicted in Figure 7.4 (c). As seen from the graph, for rGO, the removal efficiency rose sharply from 1.2% at 15 min to 75.96% after 90 min. Similar results were obtained for all the aminated graphene samples as well. It can be observed that adsorption reached equilibrium after 90 min and remained steady thereafter, indicating complete saturation and attainment of maximum efficiency. The short and rapid NAP removal observed can be attributed to the thin two-dimensional sheet-like morphology of all the samples, which provides abundant adsorption sites and short diffusion paths for NAP, thereby facilitating adsorption. However, as adsorption progresses, the active sites become occupied, resulting in fewer available sites and a slowdown in adsorption until equilibrium is attained.

Although all four aminated graphene samples outperformed the non-aminated counterpart (rGO) and exhibited the same pH-dependent trend with contact time, the $-\text{NH}_2$ -functionalized derivative Am-rGO@7 achieved the highest removal percentage. This suggests that modification with $-\text{NH}_2$ groups at neutral pH enhances NAP adsorption. Therefore, Am-rGO@7 was selected as the optimized adsorbent for all subsequent kinetic and isotherm studies.

7.3.2 Adsorption kinetics

The study of kinetics plays an important role in comprehending the mechanisms and dynamics of adsorption. In this work, the adsorption kinetics of NAP were analyzed

by examining the relationship between the amount adsorbed and contact time using different mathematical models, including the pseudo first-order model, and the pseudo-second-order reaction model. The pseudo-first-order model explains the adsorption of solute molecules onto a solid adsorbent over time, assuming that physical interactions like van der Waals forces, hydrogen bonding, and π - π interactions influence the rate-limiting step [63]. In contrast, the pseudo-second-order model characterises the adsorption process as chemical in nature, with the rate constant being proportional to the number of occupied active adsorption sites [64].

The nonlinear forms of the pseudo-first order kinetic model and pseudo-second order kinetic model are expressed as:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (7.4)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (7.5)$$

where q_e and q_t are the amount of NAP adsorbed on Am-rGO@7 in mg g^{-1} at equilibrium and at any time t (min), respectively, and k_1 is the rate constant of the first-order model (min^{-1}) and k_2 is the rate constant of the second-order model ($\text{g mg}^{-1} \text{min}^{-1}$). The fitting curves for the non linear models are presented in Figure 7.5, and the corresponding parameters are summarized in Table 7.3. It is evident that, compared to the pseudo-first-order kinetic model, the pseudo-second-order model provides a smoother fit to the experimental data, with an R^2 value of 0.987. Additionally, the equilibrium adsorption capacity derived from the pseudo-second-order model is 149.22 mg g^{-1} which is in good agreement with the experimentally obtained batch adsorption values of 144.6 mg g^{-1} . These findings suggest that the adsorption of naphthalene onto Am-rGO@7 adheres to the pseudo-second-order kinetic model, primarily governed by chemisorption [65]. This observation is consistent with previous reports on similar adsorption systems, reinforcing the conclusion that chemisorption is the rate-determining step. The applicability of pseudo-second-order model for describing NAP adsorption has also been demonstrated in previous studies. Das et al. [62] reported a good fit of this model for NAP adsorption on graphene, while Wu et al. [65] and Xiao and colleagues [66]

observed similar behaviour using walnut shell-based activated carbon and coal-based activated carbon respectively.

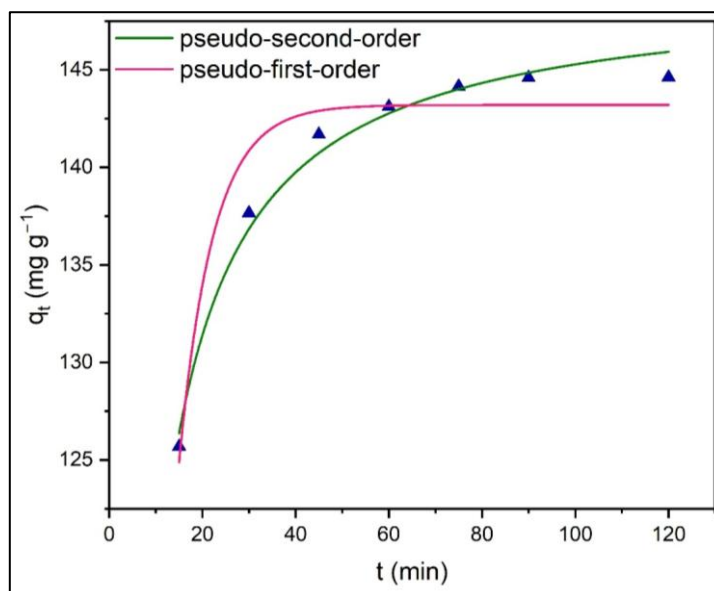


Figure 7.5. Fitting results of pseudo-first-order model and pseudo-second-order model.

Table 7.3. Kinetic parameters for NAP adsorption onto Am-rGO@7.

Adsorbate	Pseudo-first order	Pseudo-second order
	$q_t = q_e(1 - e^{-k_1 t})$	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$
Am-rGO@7	$k_1 = 0.137 \pm 0.007$	$k_2 = 0.002 \pm 1.53$
	$q_{e(cal)} = 143.20 \pm 0.8$	$q_{e(cal)} = 149.22 \pm 0.6$
	$q_{e(exp)} = 144.6$	$q_{e(exp)} = 144.6$
	$R^2 = 0.943$	$R^2 = 0.987$
	$\chi^2 = 0.025$	$\chi^2 = 0.005$

7.3.3 Adsorption isotherm

Adsorption isotherm models are widely employed to evaluate the adsorption capacity of adsorbents and to understand the interaction mechanism between the adsorbate and adsorbent. In the present study, the experimental equilibrium data were fitted to three

well-known isotherm models, namely the Langmuir, Freundlich and Temkin models, to better understand the adsorption behavior onto Am-rGO@7.

The Langmuir adsorption model assumes that adsorption occurs at specific homogeneous sites within the adsorbent, leading to the formation of a saturated monolayer of adsorbate molecules at the surface. In this model, all adsorption sites possess identical affinity for the adsorbate [67,68]. The Langmuir equation can be expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7.6)$$

where, q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate, q_m is the maximum amount of NAP adsorbed, K_L is the Langmuir adsorption constant related to the adsorption energy.

The Freundlich isotherm model, on the other hand, is based on the assumption that adsorption occurs on a non-uniform surface where the binding sites exhibit varying affinities for the adsorbate. Unlike the Langmuir model, it does not predict a saturation limit but instead suggests that adsorption can occur in multiple layers. It is represented by:

$$q_e = K_F C_e^{1/n} \quad (7.7)$$

where, K_L ($\text{mg g}^{-1} (\text{mg L}^{-1})^n$) is the Freundlich constant indicative of adsorption capacity.

The Temkin isotherm model assumes that due to the indirect adsorbate–adsorbate interactions effect, the heat of adsorption decreases linearly with surface coverage due to these interactions. The model is expressed as:

$$q_e = B \ln(K_T C_e) \quad (7.8)$$

where, K_T (L mg^{-1}) is the Temkin equilibrium binding constant, $B (= \frac{RT}{b})$ is a constant related to the heat of adsorption, with R being the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is temperature (K).

The adsorption isotherm fitting profiles are depicted in Figure 7.6 (a), and the related fitting parameters are compiled in Table 7.4. Among the three tested models, the Langmuir isotherm provided the most accurate representation of the experimental data, with correlation coefficients (R^2) of 0.988, while the Freundlich and Temkin models produced lower R^2 values of 0.852 and 0.897 respectively. The fit for Langmuir also corroborates with the reduced chi-square values. This can be attributed to the fact that, although the surface of Am-rGO@7 contains a combination of sp^2 domains, sp^3 defects, and nitrogen- and oxygen-containing functional groups, adsorption is dominated by π - π interactions with the sp^2 graphitic regions. As a result, these domains act as the primary binding sites for NAP, making the adsorption behavior effectively resemble that on a homogeneous surface. The maximum adsorption capacity calculated from the Langmuir model was found to be ~ 251 mg g^{-1} , which is in good agreement with the experimentally determined value as discussed earlier.

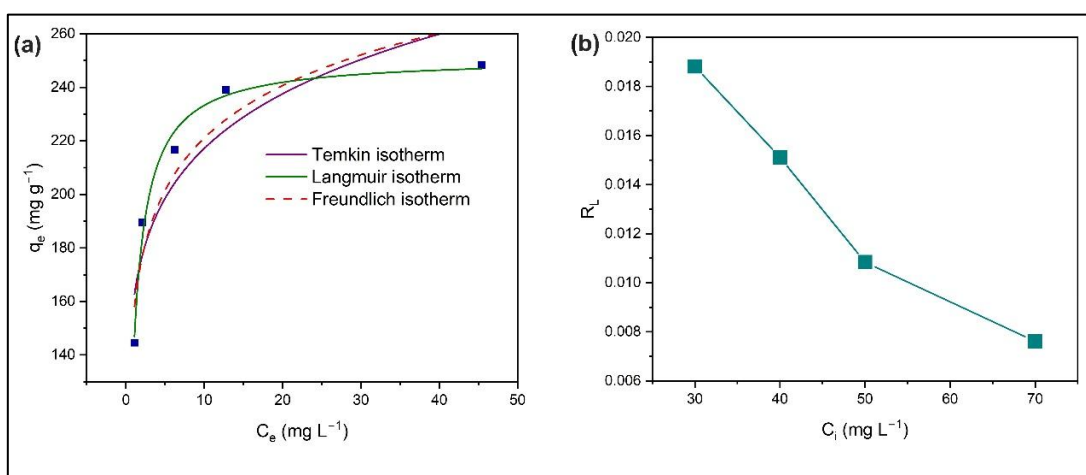


Figure 7.6. (a) Adsorption isotherms of NAP adsorption by Am-rGO@7 and fitting results using Langmuir, Freundlich and Temkin models. (b) separation factors' (R_L) plot (initial NAP concentration 30, 40, 50 and 70 mg/L; Am-rGO@7 10 mg; pH 7).

Moreover, since the adsorption of naphthalene follows the Langmuir isotherm model, the efficiency of the process can be evaluated using the dimensionless separation factor (R_L), which is calculated as [69]:

$$R_L = \frac{1}{1 + K_L C_i} \quad (7.9)$$

where, C_i is the initial concentration of NAP.

The value of R_L provides insight into the nature of adsorption where, values between 0 and 1 indicate favorable adsorption, $R_L = 1$ corresponds to linear adsorption, $R_L > 1$ denotes unfavorable adsorption, and $R_L = 0$ represents irreversible adsorption. In this study, R_L values for NAP at all tested concentrations were found to lie between 0 and 1 (Figure 7.6 (b), Table 7.4), indicating that the adsorption process is highly favourable.

Table 7.4. Parameters of Naphthalene Adsorption by Am-rGO@7.

Isotherm Models	Parameters
Langmuir model $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$ $R_L = \frac{1}{1 + K_L C_i}$	$q_m = 251.14 \pm 4.60$ $K_L = 1.304 \pm 0.11$ $R_L = 0.024 - 0.010$ $R^2 = 0.988$ $\chi^2 = 0.16$
Freundlich model $q_e = K_F C_e^{1/n}$	$n = 7.72 \pm 12.40$ $K_F = 161.17 \pm 12.40$ $R^2 = 0.852$ $\chi^2 = 1.91$
Temkin model $q_e = B \ln(K_T C_e)$	$K_T = 249.48$ $R^2 = 0.897$ $\chi^2 = 1.33$

7.3.4 Role of functional groups on NAP adsorption

Literature suggests that the adsorption process is strongly influenced by the nature of surface functional groups, which in turn play a critical role in determining the overall effectiveness of carbonaceous materials as adsorbents [30–33].

Based on this understanding, DFT studies were carried out to explore how different surface functional groups influence the adsorption of NAP. Gaining such insights can ultimately help in designing more efficient and targeted adsorbent materials. Figure

7.7 illustrates the optimised geometries and the associated adsorption energies for each surface.

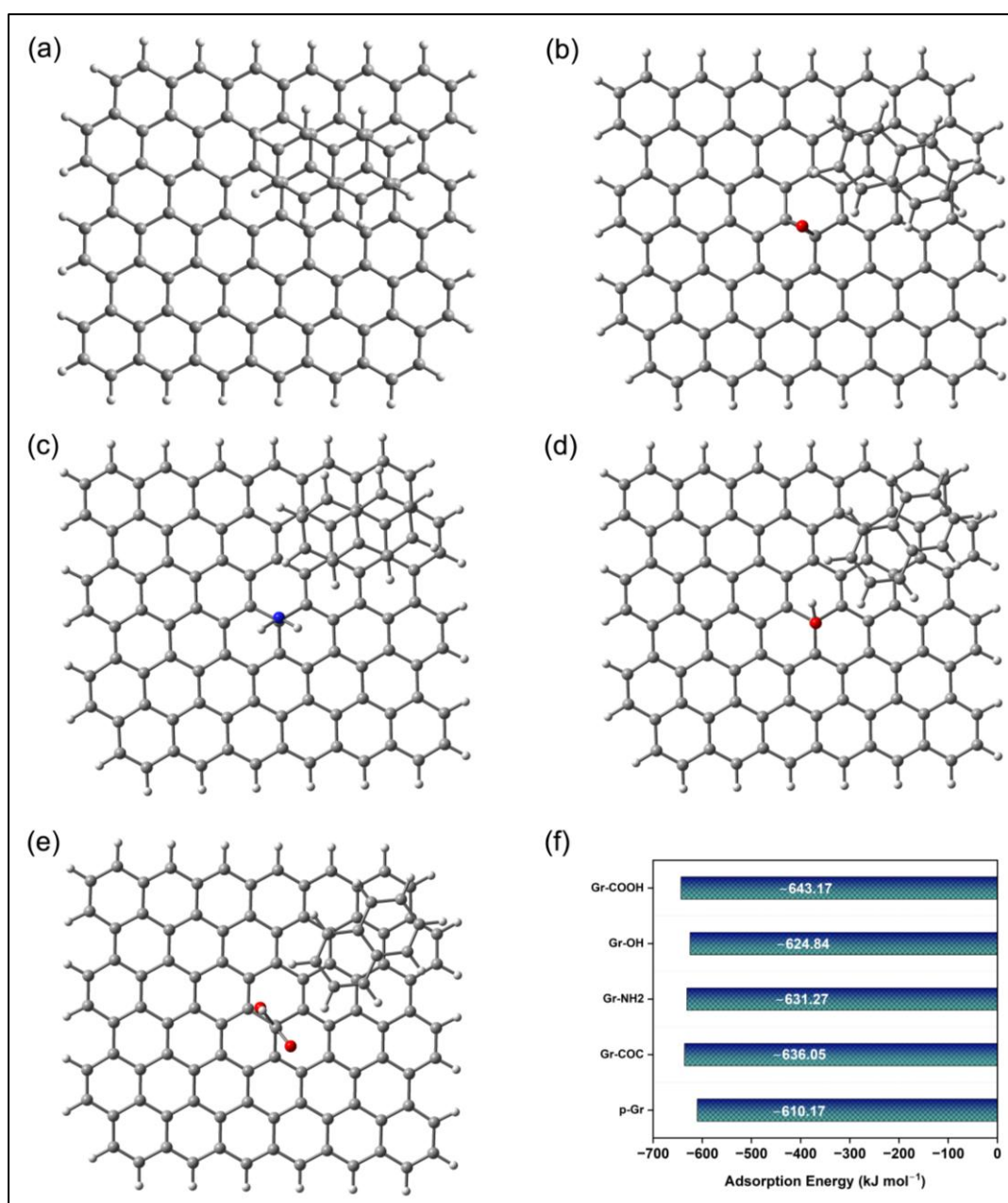


Figure 7.7. Optimised structures of NAP adsorbed on (a) p-Gr. (b) Gr-COC. (c) Gr-NH₂. (d) Gr-OH (e) Gr-COOH. (f) Comparison of adsorption energies on functionalized and unfunctionalized graphene surfaces.

Adsorption energy calculation

The influence of functional groups on NAP adsorption was evaluated through binding energy calculations. A comparison of the calculated adsorption energies revealed the interaction strength between NAP molecules and different functionalized graphene surfaces, thereby identifying the groups that exhibit the strongest adsorption affinity. Pristine (unfunctionalized) graphene (p-Gr) exhibited the weakest interaction with NAP, with an adsorption energy of approximately $-610.17 \text{ kJ mol}^{-1}$, which can be attributed primarily to π - π stacking interactions between the graphene surface and the aromatic rings of the NAP molecule. Upon functionalization, the adsorption energies became more negative, indicating stronger interactions. Among the four functional groups investigated, the $-\text{COOH}$ group exhibits the strongest interaction, with an adsorption energy of $-643.17 \text{ kJ mol}^{-1}$ (Figure 7.7 (f)). This is probably due to the synergistic action of π - π stacking, n - π EDA interactions between naphthalene's π -system and the carboxyl oxygen lone pairs, and dual hydrogen bonds from the oxygen of $-\text{COOH}$. Upon adsorption, the NAP molecule is positioned in close proximity to the oxygen atom of the $-\text{COOH}$ group, primarily due to the formation of a hydrogen bond. The distance between the nearest hydrogen atom of NAP and the oxygen atom of the $-\text{COOH}$ group is $2.42 \text{ \AA}$.

In case of Gr-COC, the presence of C-O-C linkages introduces dipoles on the graphene basal plane, as evidenced by a dipole moment of 2.617 Debye for Gr-COC compared to 0 Debye for p-Gr, thereby enhancing electrostatic interactions with the π -electron system of NAP. Furthermore, the high electronegativity of the epoxide oxygen withdraws electron density from adjacent carbon atoms, creating partially positive sites that promote charge-transfer interactions with the electron-rich NAP molecule. Additionally, although relatively weak, $\text{CH}\cdots\text{O}$ hydrogen bonds between the C-H groups of NAP and the oxygen atoms of the epoxide can contribute further stabilisation to the adsorption complex. As a result, Gr-COC exhibits an adsorption energy of $-636.05 \text{ kJ mol}^{-1}$, with the shortest distance between a NAP hydrogen and the epoxide oxygen measuring $2.76 \text{ \AA}$. The hydroxyl groups in Gr-OH, on the other hand, improve the adsorption energy by $\sim -14.67 \text{ kJ mol}^{-1}$, with π - π stacking as the

dominant interaction and secondary contributions from hydrogen bonding and $n-\pi$ EDA interactions via the oxygen lone pairs.

In case of Gr-NH₂, E_{ad} is nearly equal to that of Gr-COC and higher than that of Gr-OH, indicating that amine functionalization enhances NAP adsorption. The grafted -NH₂ group introduces greater basicity, resulting in stronger interactions with NAP compared to pristine graphene [70]. In this system, $\pi-\pi$ stacking, $n-\pi$ EDA interactions, and hydrogen bonding collectively contribute to the adsorption behaviour. However, the hydrogen bonding is weaker than that observed in Gr-COOH, leading to a slightly higher adsorption energy. Even so, Gr-NH₂ achieves an E_{ad} of $-631.27 \text{ kJ mol}^{-1}$, compared to $-610.17 \text{ kJ mol}^{-1}$ for p-Gr. Additionally, the shortest distance between a hydrogen atom of NAP and the nitrogen atom of the -NH₂ group is 2.65 Å, which is longer than the corresponding distances in Gr-COOH and Gr-COC, likely due to the lower electronegativity of nitrogen relative to oxygen in the other functional groups. Thus, the incorporation of various functional groups onto graphene's surface significantly enhances the overall adsorption process by introducing additional attractive forces beyond pure $\pi-\pi$ interactions. This not only increases the number of active sites available for adsorption but also improves the affinity of the adsorbent. Furthermore, while functional groups such as -COOH, -OH, and -COC are commonly present on graphene surfaces obtained through chemical exfoliation, the incorporation of amine functionalities introduces additional active sites that enhance adsorption interactions. As a result, aminated graphene samples exhibit stronger adsorption compared to non-aminated counterparts. The -NH₂ groups facilitate hydrogen bonding as well as stronger electrostatic and van der Waals interactions, thereby increasing the overall adsorption energy. With increasing amine concentration, more active sites become available, leading to progressively higher adsorption energies. This trend is in excellent agreement with the experimental observations reported earlier, where samples with higher nitrogen content demonstrated superior adsorption performance. Thus, the computational results clearly validate that amine functionalization plays a crucial role in amplifying the adsorption strength of graphene-based materials.

Non-covalent interactions

The RDG analysis is a powerful and visually intuitive method for identifying non-covalent interactions, particularly weak intermolecular forces. Accordingly, RDG analysis was performed to systematically visualise and characterise the non-covalent interactions between the adsorbents and NAP (Figure 7.8). In the RDG theory proposed by Johnson and colleagues, the RDG (defined as $s = 1/(2(3\pi^2)^{1/3})|\nabla\rho|\rho^{4/3}$) serves to characterise deviations from a homogeneous electron distribution [71]. Within this framework, large negative values of $\text{sign}(\lambda_2)\rho$ indicate attractive interactions, whereas large positive values correspond to repulsive interactions.

The scatter plots correlate the RDG with the product of $\text{sign}(\lambda_2)\rho$. Points falling at large negative values of $\text{sign}(\lambda_2)\rho$ correspond to strong attractive interactions (e.g., hydrogen bonds), those clustered near zero reflect weak van der Waals forces, and those at large positive values indicate steric repulsion. Each of these interactions is colour-coded in both the scatter map and the RDG isosurface (Figure 7.8 (f)). By matching colours between the two plots, one can pinpoint where each type of interaction occurs, so we discuss the relationship between the two kinds of graphs by region of various colours. Figure 7.8 presents the RDG isosurfaces (left and middle figures) alongside their matching colour-coded scatter plots (right) for all systems.

As illustrated in Figure 7.8, green isosurfaces appear in the region between the NAP molecule and the graphene surfaces, suggesting that the interaction is relatively weak and predominantly governed by van der Waals forces. In addition, red coloured shuttle-shaped isosurfaces are observed at the centres of the six-membered rings in both various graphene surfaces and NAP, indicating pronounced steric effects within the aromatic cores. Similar shuttle-like isosurfaces are also present between adjacent C–H bonds along the graphene edges, exhibiting a combination of green and orange regions. The appearance of orange isosurfaces corresponds to a spike at approximately 0.013 in the RDG scatter diagram, representing weak repulsive interactions and the red isosurfaces are associated with a spike near 0.02, which is indicative of stronger steric repulsion.

Similarly, the RDG colour-filled scatter plots (Figure 7.8) indicate that the interaction between NAP and the adsorbents is weak. In all functionalized graphene samples, the spike at ~ -0.014 in the scatter diagram reflects weak hydrogen-bonding interactions, whereas in pristine graphene it signifies π - π stacking between the aromatic ring of NAP and the graphene surface. Additionally, a green spike around ~ -0.06 along with spikes within the range of 0.03 to 0.006, represented in green and light brown in the scatter plots, correspond to regions on the RDG isosurface indicative of weak attractive forces and mild steric repulsion, respectively.

To better understand the influence of various functional groups on the adsorption behaviour of NAP, it is essential to examine the features representing both attractive and repulsive interactions. Comparison of the attractive interaction spikes at ~ -0.014 and -0.06 reveals that these features are broader and more pronounced, both in spike intensity and distribution in the Gr-COOH, followed sequentially by Gr-COC, Gr-NH₂, Gr-OH, and p-Gr. This trend indicates that the strength of intermolecular interactions follows the order: -COOH > -COC > -NH₂ > -OH > pristine.

Furthermore, analysis of the repulsive force spikes in the range of ~ -0.013 -0.02 shows the largest distribution for p-Gr, followed by Gr-OH, Gr-NH₂ $\approx$ Gr-COC, and Gr-COOH. These results reinforce the conclusion that functionalization, particularly with electron-donating or hydrogen-bonding groups, reduces steric hindrance and enhances adsorption strength. The overall trend in intermolecular attractive forces, as deduced from both the RDG scatter plots and isosurface images, is consistent with the calculated adsorption energies and confirms the order: Gr-COOH > Gr-COC > Gr-NH₂ > Gr-OH > p-Gr.

Moreover, as the amine content increases, the attractive interactions is expected to become stronger. This is reflected in the adsorption capacity, which reaches its maximum for the NH₂-rGO@7 sample, corresponding to the highest amine concentration, and gradually decreases with lower amine content. These findings align well with experimental results, confirming the direct relationship between amine concentration and NAP removal efficiency.

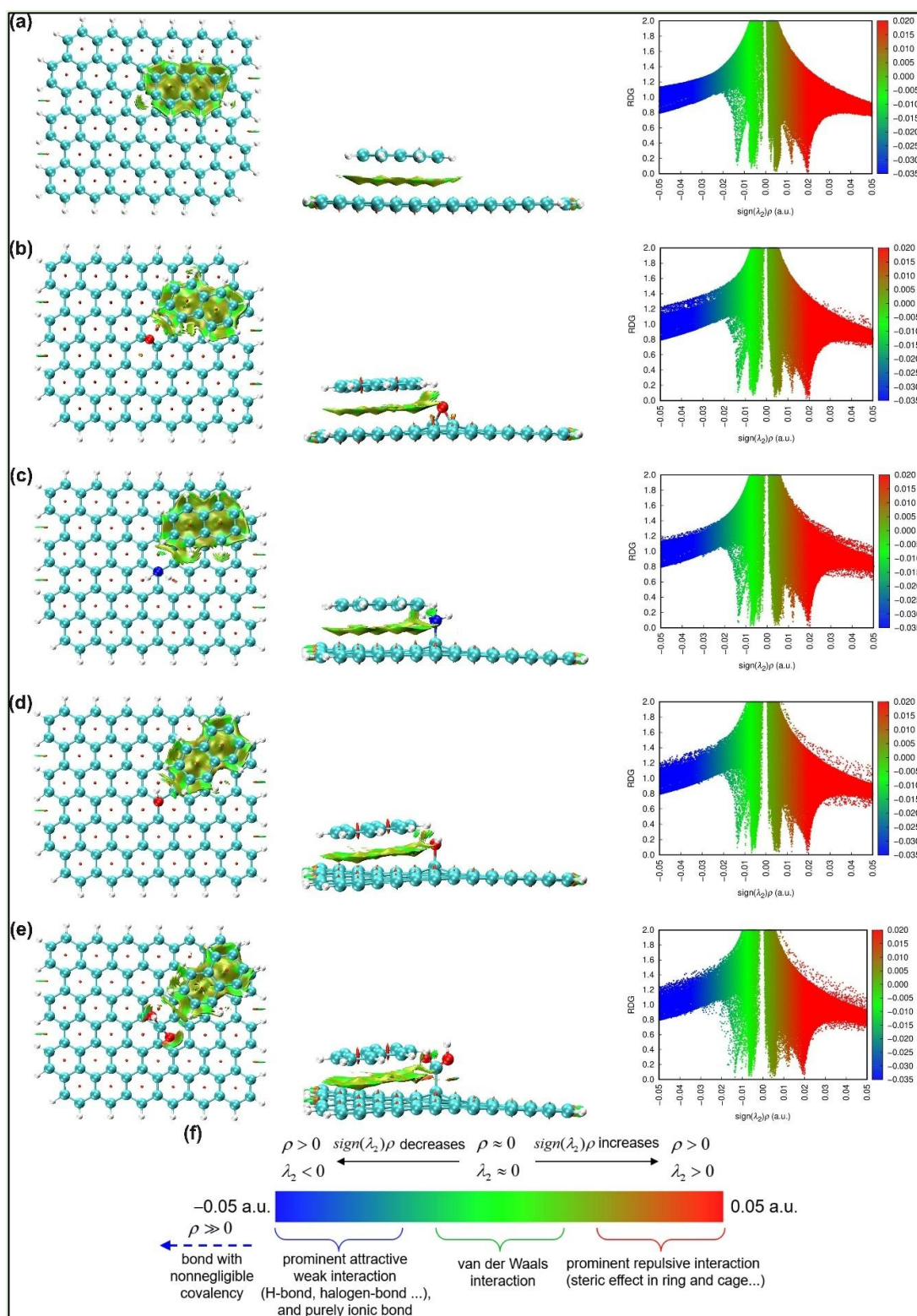


Figure 7.8. Colour-filled reduced density gradient isosurfaces (left and middle) for the optimised conformations alongside their corresponding RDG scatterplots (right)

of (a) p-Gr. (b) Gr-COC. (c) Gr-NH₂. (d) Gr-OH (e) Gr-COOH. (f) Interpretation guide for the figure's colour scheme.

7.3.5 Comparison with other adsorbents

Table 7.5 provides a summary of various adsorbents previously reported for the removal of NAP from aqueous solutions. It is important to note that these studies were conducted under varying experimental conditions, such as differences in adsorbent dosage and initial NAP concentration. Nevertheless, the adsorbents utilised in the present study demonstrate superior removal efficiencies compared to those reported in the literature.

Table 7.5: Comparative evaluation of the adsorption efficiency of various adsorbents for NAP removal.

Adsorbent	Maximum adsorption capacity (mg g⁻¹)	Removal %	Equilibrium (mins)	Ref.
AC modified with nitric acid	90.91	91.97	20	[72]
Bentonite	--	39.2	90	[73]
Clinoptilolite	2.72	65	30	[61]
AC from petroleum coke	3.2	--	420	[74]
Clinoptilolite	1.63	81.67	60	[75]
APTES-MCM- 41 from rice husk ashes	0.12	81.20	1440	[76]
MCM-41 from rice husk ashes	0.13	79.94	1440	[77]
Surfactant- modified	2.60	70	1440	[78]

mesoporous silica				
rGO	114.45	76.3	90	This Work
Am-rGO@7	144.65	96.43	90	This Work

7.4. Conclusion

This work demonstrates that aminated reduced graphene oxide, synthesised via a simple, moderate-temperature process, serves as an efficient adsorbent for NAP removal from aqueous media. A comprehensive investigation of process parameters, including adsorbent dosage, solution pH, and contact time, was carried out. Among the tested materials, Am-rGO@7 exhibited the highest performance, achieving a maximum removal efficiency of 96.4 % and an adsorption capacity of 144.65 mg g⁻¹ under neutral conditions. Furthermore, density functional theory (DFT) calculations were employed to evaluate the influence of various surface functional groups on adsorption behavior. Carboxyl (–COOH) and epoxide (–COC) groups offered the strongest binding, but amine (–NH₂) functionalities still conferred substantially enhanced affinity, validating the experimental choice of aminated surfaces. The systematic correlation between amine content, adsorption energy, and removal efficiency highlights the importance of tuning graphene's surface chemistry for pollutant specificity. Based on its simple synthesis and high adsorption performance, aminated graphene presents a scalable and promising platform for water purification applications targeting NAP and potentially other PAHs.

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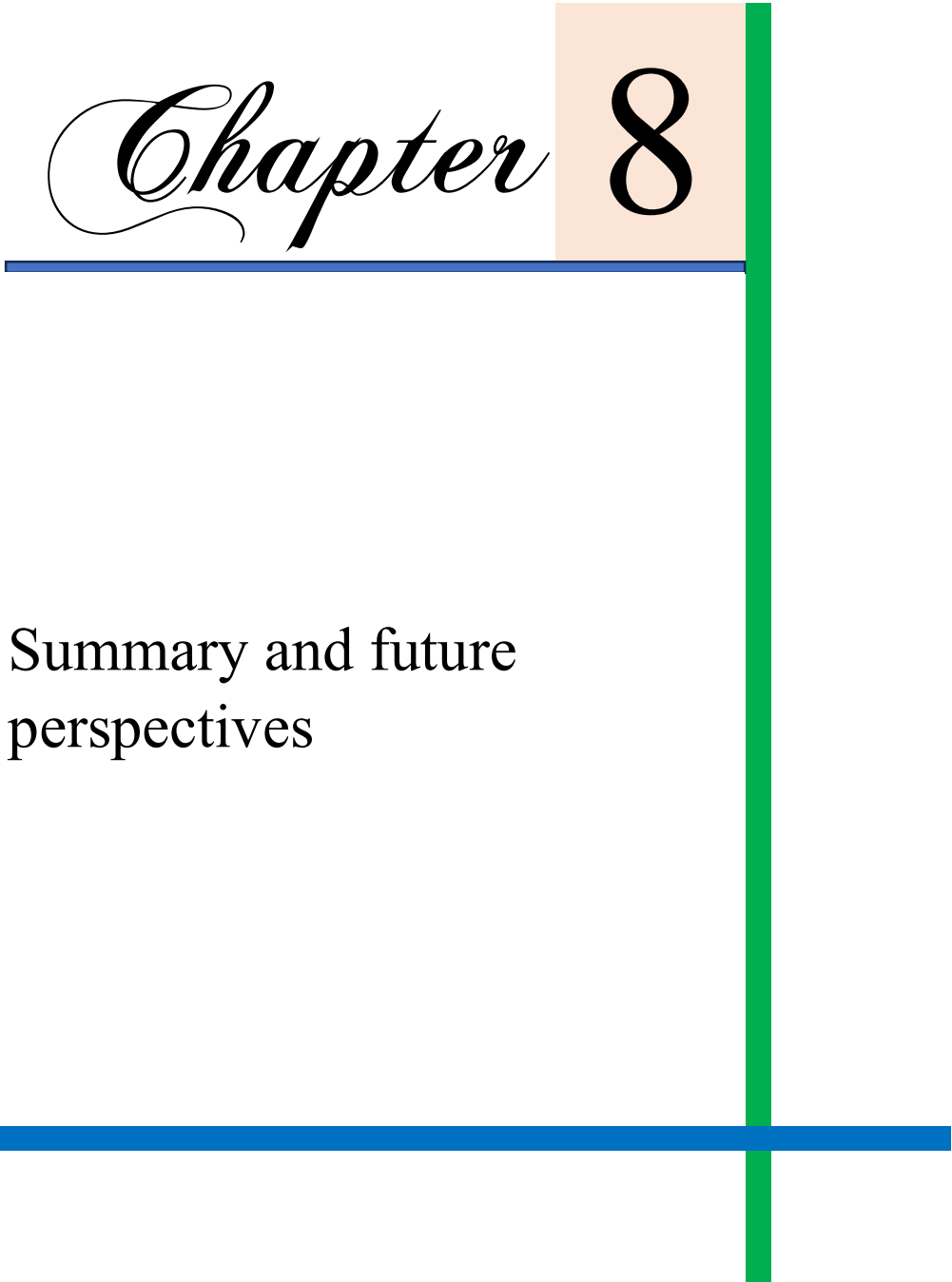
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Chapter 8



Summary and future
perspectives

CHAPTER 8

Summary and future perspectives

8.1 Summary

This thesis presents a comprehensive and systematic investigation into the atomic-level engineering of graphene through controlled heteroatom doping and surface functionalization, with the objective of enhancing its electronic, optical, electrochemical, and adsorption performance. Although graphene possesses extraordinary intrinsic properties such as high electrical conductivity, large theoretical surface area, and excellent mechanical strength, its practical implementation in energy storage and environmental remediation systems remains limited by issues including restacking tendencies, limited pseudocapacitive behaviour, and insufficient chemical specificity toward pollutants. Addressing these limitations requires deliberate structural modification at the atomic and molecular levels in order to tailor graphene's surface chemistry, defect density, and interfacial characteristics.

In this context, the present work adopts an integrated approach combining density functional theory (DFT) modeling with rapid, scalable, and environmentally benign experimental synthesis strategies to establish clear structure–property–performance correlations in graphene-based systems. The research systematically investigates (i) platinum group element doping of graphene to modulate its structural, electronic, and optical characteristics; (ii) a scalable amination strategy for graphene aimed at enhancing electrochemical charge storage performance; (iii) the green and rapid synthesis of brominated graphene and its influence on electrochemical behaviour, along with a comparative evaluation of bromination efficiencies of various tribromide reagents ; (iv) simultaneous dual functionalization with bromine and amine groups to achieve synergistic enhancement in capacitive performance; and (v) surface chemistry tuning for efficient adsorption of organic pollutants from aqueous environments. By correlating theoretical predictions with experimental validation, this thesis demonstrates how rational atomic-scale engineering can transform graphene into a multifunctional material platform suitable for high-performance supercapacitors, regenerative energy capture systems, and water purification technologies. The summary of the overall thesis work is presented below:

1. The computational component of this study examined the effect of platinum group element (PGE) doping (Ru, Rh, Pd, Os, Ir, and Pt) on pristine graphene using the B3PW91/LANL2DZ level of theory. Formation energy calculations indicated that although doping slightly reduces thermodynamic stability, the graphene framework remains structurally viable, following the order: p-Gr > Gr-Os > Gr-Ru > Gr-Ir > Gr-Rh > Gr-Pt > Gr-Pd. Structural analysis revealed significant lattice distortions, where bond lengths in doped systems varied between 1.89–1.96 Å compared to 1.96 Å in pristine graphene, and bond angles decreased drastically from 120° in p-Gr to 85.83°–95.11° after doping. Electronic structure calculations showed substantial narrowing of the HOMO–LUMO energy gap from 4.070 eV in pristine graphene to 2.126–2.900 eV in doped systems, confirming enhanced electronic conductivity. Density of states (DOS) analysis further demonstrated a downward shift in Fermi level and a pronounced increase in states near the Fermi energy, particularly for Ru- and Os-doped graphene, indicating improved charge carrier availability. Time-dependent DFT calculations revealed shifts in maximum absorption wavelength (λ_{max}) from 294.55 nm in pristine graphene to a broadened range of 291.70–478.76 nm in doped systems, confirming tunable optical behaviour. Collectively, these theoretical findings validate PGE doping as an effective strategy for modulating graphene's electronic band structure and optical response.

2. A rapid and scalable one-pot synthesis route was developed for aminated reduced graphene oxide (NH₂-rGO), completing the entire process within approximately 9 hours. By tuning the pH of the reaction medium, nitrogen incorporation was controlled, achieving up to ~6 atomic % nitrogen as confirmed by XPS analysis. Deconvolution of the N 1s spectrum verified that primary amine groups were the dominant nitrogen species, with minimal formation of pyridinic or other nitrogen configurations. FTIR spectra exhibited characteristic N–H stretching and bending vibrations, further confirming successful amination. Elemental mapping revealed uniform nitrogen distribution across the graphene matrix.

The electrochemical performance of NH₂-rGO demonstrated remarkable enhancement compared to rGO. In a three-electrode configuration, the aminated

material exhibited significantly improved capacitive behaviour. Most notably, the symmetric supercapacitor device (A-7 SSC) achieved a specific capacitance of 322 F g^{-1} at 1 A g^{-1} , representing nearly a five-fold increase compared to rGO SSC. The gravimetric energy density reached 54.18 Wh kg^{-1} at 1 A g^{-1} , compared to only 10.77 Wh kg^{-1} for rGO, while the volumetric energy density improved to 48.16 Wh L^{-1} , approximately seven times higher than rGO (6.89 Wh L^{-1}). These enhancements are attributed to improved wettability, increased electrochemically active sites, and pseudocapacitive contributions from amine functionalities. The results clearly demonstrate that controlled nitrogen functionalization substantially enhances charge storage capability and establishes $\text{NH}_2\text{-rGO}$ as a highly promising electrode material for advanced supercapacitors.

3. A major advancement presented in this thesis is the development of a rapid and environmentally benign bromination strategy for reduced graphene oxide (rGO), overcoming the limitations of conventional bromination protocols that rely on toxic reagents such as liquid bromine or hydrobromic acid and often require extended reaction times exceeding 24 hours.

In the present study, tetrabutylammonium tribromide (TBATB) was employed as a greener brominating agent, enabling complete bromination of rGO within just 60 minutes under mild reaction conditions. This represents one of the fastest reported bromination approaches for graphene derivatives. XPS analysis confirmed successful bromine incorporation with a bromine content of 4.73%, while FTIR spectra exhibited a characteristic C–Br stretching vibration near 590 cm^{-1} , validating covalent functionalization. Structural analysis through XRD revealed that the interlayer spacing remained largely unchanged after bromination, indicating that bromine atoms were covalently attached to the graphene surface rather than intercalated between layers. FESEM and HRTEM images showed the retention of a wrinkled, sheet-like morphology, and elemental mapping confirmed uniform bromine distribution throughout the graphene matrix.

The electrochemical performance of brominated graphene demonstrated substantial enhancement compared to pristine rGO. A symmetric supercapacitor fabricated using

bromographene (BG-20 SSC) delivered a specific capacitance of 148.6 F g^{-1} , corresponding to an approximately 230% improvement over rGO (44.93 F g^{-1}). The device achieved a gravimetric energy density of 46.44 Wh kg^{-1} at a power density of 750 W kg^{-1} , representing an 84.8% increase compared to the rGO-based device ($25.125 \text{ Wh kg}^{-1}$). Furthermore, the bromographene supercapacitor exhibited excellent cycling stability, retaining 91.67% of its initial capacitance after 10,000 GCD cycles.

Building upon this optimized bromination strategy, a comparative investigation of five environmentally benign tribromide reagents, TEATB, TPATB, TBATB, CTMATB, and CetPyTB was conducted to evaluate their bromination efficiency and bonding characteristics. XPS quantification revealed bromine contents of 5.62%, 5.37%, 4.73%, 9.38%, and 5.19% for TEATB@rGO, TPATB@rGO, TBATB@rGO, CTMATB@rGO, and CetPyTB@rGO, respectively. Among these, CTMATB@rGO exhibited the highest bromine incorporation ($\sim 9.38 \text{ at.}\%$ by XPS and $\sim 20 \text{ wt.}\%$ by EDS), demonstrating superior functionalization efficiency. Deconvolution of the Br 3d spectra indicated that CTMATB@rGO possessed the highest fraction of covalently bonded bromine (97.02%), with negligible oxybrominated species, whereas TPATB@rGO, TEATB@rGO, CetPyTB@rGO, and TBATB@rGO showed 70.83%, 85.83%, 90.02%, and 14.44% covalent bromine bonding, respectively.

Additionally, due to the ammonium-based nature of the tribromides, partial nitrogen incorporation was observed, with nitrogen contents of 1.57%, 1.75%, 4.68%, 2.14%, and 0.59% for TEATB@rGO, TPATB@rGO, TBATB@rGO, CTMATB@rGO, and CetPyTB@rGO, respectively. These findings indicate that tribromide selection plays a crucial role not only in bromine incorporation but also in controlling the extent of covalent bonding and co-functionalization. Overall, this comparative study establishes CTMATB as the most efficient green brominating agent among those investigated and demonstrates that environmentally benign tribromides provide a rapid, scalable, and effective route for graphene functionalization, while simultaneously generating reactive C–Br sites suitable for further chemical transformations.

4. This thesis further demonstrates a synergistic dual-functionalization strategy involving the simultaneous incorporation of bromine and nitrogen functionalities onto reduced graphene, leading to the formation of dual-functionalized graphene (DFG). This approach was designed to combine the electron-withdrawing nature of bromine with the electron-donating and pseudocapacitive characteristics of nitrogen, thereby optimizing both electronic structure and electrochemical activity. XPS analysis revealed a bromine content of approximately 9.38 at.% in the DFG material, with Br 3d deconvolution indicating that ~97.02% of the bromine was covalently bonded, while only ~2.98% existed as physisorbed Br^- species. Simultaneously, N 1s deconvolution confirmed that amine-type nitrogen species were predominant after functionalization, establishing successful dual incorporation. Elemental mapping demonstrated uniform spatial distribution of both bromine and nitrogen across the graphene surface, while Raman spectroscopy indicated that vacancy-type defects dominated the defect structure, contributing additional electrochemically active sites.

The electrochemical performance of the dual-functionalized graphene exhibited significant enhancement compared to RG. Surface transformation from RG to DFG resulted in a 134% increase in specific capacitance, highlighting the strong synergistic interaction between bromine- and nitrogen-induced active sites. At a power density of 800 W kg^{-1} , the DFG-based supercapacitor delivered a 149.6% improvement in energy density relative to RG. Electrochemical impedance spectroscopy further revealed a noticeable reduction in both solution resistance and charge-transfer resistance, indicating improved ion transport kinetics and faster electron mobility arising from optimized surface chemistry. The device also demonstrated outstanding cycling stability, exhibiting only a marginal 1.19% loss in capacitance after 10,000 charge–discharge cycles at a high current density of 10 A g^{-1} , confirming excellent structural robustness under prolonged operation.

A notable advancement of this work is the evaluation of temperature-dependent electrochemical behaviour. The DFG-based supercapacitor operated reliably over a wide temperature range from -15°C to 100°C , maintaining nearly constant electrochemical performance without significant degradation. Such a broad

operational window underscores the thermal stability of DFG SC for real-world applications under extreme environmental conditions.

To further validate practical applicability, a proof-of-concept demonstration was performed by integrating the DFG-based supercapacitor into a regenerative braking energy capture system. The device successfully stored electrical energy generated during braking events, illustrating its capability for rapid charge–discharge cycles and high power delivery. The combined attributes of high specific capacitance, superior energy–power characteristics, minimal long-term degradation, and wide thermal tolerance establish DFG SC as a highly promising candidate for next-generation high-performance supercapacitors, particularly in applications such as electric vehicles and energy recovery systems.

5. In addition to its applications in energy storage, this thesis also highlights the potential of surface-modified graphene for environmental remediation, particularly for the removal of naphthalene (NAP) from water. Aminated reduced graphene oxide was evaluated as an adsorbent and a systematic study was carried out to understand the effect of different experimental parameters, including adsorbent dosage, solution pH, and contact time, on the removal efficiency.

Among the synthesized materials, Am-rGO@7 exhibited superior performance, achieving a maximum removal efficiency of 96.4% and an adsorption capacity of 144.65 mg g⁻¹ under neutral pH conditions. The high adsorption capacity is attributed to the synergistic interaction between π – π stacking of the aromatic graphene framework and the hydrogen bonding/electrostatic interactions introduced by amine functionalities.

To better understand the adsorption process at the molecular level, density functional theory (DFT) calculations were also carried out. These calculations were used to study how different surface functional groups on graphene interact with naphthalene molecules. The results showed that functional groups play an important role in determining adsorption strength. Although carboxyl (–COOH) and epoxide (–COC) groups showed strong interactions, the presence of amine (–NH₂) groups significantly

enhanced the adsorption capability compared to unmodified graphene. The theoretical findings were consistent with the experimental results, confirming that introducing nitrogen-containing groups improves adsorption performance. This combined experimental and theoretical study demonstrates that controlled surface functionalization not only enhances electrochemical properties but also improves the adsorption efficiency of graphene-based materials.

8.2 Future directions

The results presented in this thesis open several meaningful directions for future research and practical development of functionalized graphene materials. One logical next step is to combine aminated or brominated graphene with other two-dimensional materials such as layered double hydroxides (LDHs), transition metal dichalcogenides (TMDs), or MXenes. Forming such heterostructures could improve charge transfer at the interface, facilitate faster ion movement, and enhance structural stability. This approach may help in achieving supercapacitors with higher volumetric energy density, especially for compact and miniaturized energy storage systems. Further, to move closer to real-world applications, future work should also focus on device-level optimization. This includes improving electrode design, exploring binder-free configurations, and testing gel or solid-state electrolytes. Developing asymmetric or hybrid supercapacitor systems could further increase energy density while maintaining high power performance and long cycling life. Such efforts would help translate laboratory-scale results into practical energy storage devices.

From an environmental point of view, the adsorption performance of aminated graphene can be extended beyond naphthalene to other polycyclic aromatic hydrocarbons (PAHs) as well as emerging pollutants such as pharmaceuticals and persistent organic contaminants. In addition, computational studies suggest that brominated graphene may show strong interactions with heavy metal ions such as mercury. This indicates that brominated graphene could be further explored as a selective material for heavy metal removal from contaminated water. Additionally, it will be important to test the adsorption performance in real wastewater samples rather than only in model laboratory solutions. Studying the effects of competing ions,

varying pH conditions, and complex water matrices will provide a more realistic understanding of material performance.

From a theoretical perspective, more detailed density functional theory (DFT) studies can be carried out to better understand adsorption pathways, charge redistribution, and the role of defects in governing material performance. Such investigations would provide deeper insight into how different functional groups influence electronic structure and surface interactions. These computational findings can then be used to guide the rational design of graphene materials with tailored surface chemistry for specific electrochemical and environmental applications. Combining theoretical predictions with careful experimental validation will remain essential for developing more efficient and application-ready graphene-based systems in the future.

Appendices

Appendix-1

Plagiarism reports

Appendix-2

List of publications

Appendix-3

List of patents

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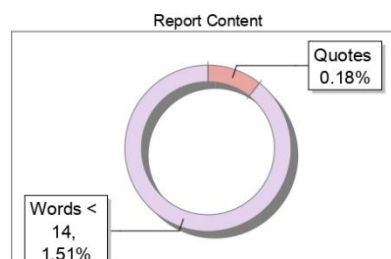
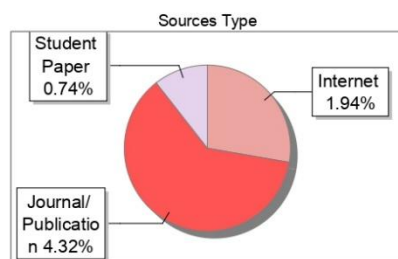
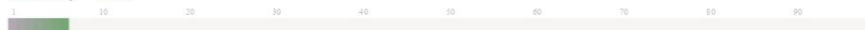
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Article

Scalable one-pot synthesis of aminated reduced graphene oxide for high-performance supercapacitor electrodes

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SUMMARY

Functionalizing graphene by adding amine groups can significantly enhance its wettability and overall properties. However, traditional methods for introducing $-NH_2$ typically require lengthy processing times, high temperatures, and pressures, which limit their suitability for large-scale production. This work presents the fastest method reported to date for synthesizing aminated reduced graphene oxide (NH_2 -rGO) under moderate temperatures, completing the entire process in just ~ 9 h. The nitrogen content of the NH_2 -rGO is tunable from 2 to 6% and the material also exhibits excellent electrochemical properties. A symmetric supercapacitor based on the prepared material demonstrated a specific capacitance of 322 F g^{-1} at 1 A g^{-1} , which is a 5-fold increase compared to rGO. It also delivered an impressive volumetric energy density of 48.16 Wh L^{-1} , which is nearly seven times higher than rGO (6.89 Wh L^{-1}). Further, NH_2 -rGO could also be utilized in biosensing, photovoltaics, catalysis, and as a base for further chemical modifications.

INTRODUCTION

The increasing reliance on non-renewable energy sources, from individual households to large-scale industries, highlights the pressing need for advanced energy storage solutions. These devices enable efficient storage of energy from renewable sources, such as sunlight, wind, ensuring its availability for future use. Despite variations in their methods of storing and delivering energy, most energy storage devices share a common purpose: to store charge.¹ Among these, supercapacitors stand out for their ability to rapidly store and discharge energy.² Supercapacitors store energy through two main mechanisms: electrical double-layer (EDL) capacitance and pseudocapacitance. EDL capacitors utilize electrode materials with a high surface area, where energy is stored through the accumulation of charges at the interface between the electrode and electrolyte. Since EDL-based supercapacitors do not involve physical changes in the electrodes during operation, they can sustain millions of charge and discharge cycles with minimal degradation in performance.² Pseudocapacitors, on the other hand, store energy via reversible Faradaic redox reactions. Materials with pseudocapacitive properties, such as MXenes, polyaniline offer significantly higher energy densities compared to EDL-based supercapacitors. However, the Faradaic reactions occurring in pseudocapacitive electrodes can cause phase changes, which may reduce their lifespan and power density.^{3,4} Additionally, EDL capacitors

have faster response times compared to pseudocapacitors, making them better suited for applications that require rapid energy storage and release.⁴

A highly promising electrode material for EDL capacitors is graphene, a 2D allotrope of carbon with sp^2 -hybridized carbon atoms arranged in a hexagonal lattice.⁵ Its exceptional optical, mechanical, and electrical properties have generated significant interest, fueling the advancement of numerous applications.^{2,6} These include drug delivery,⁷ biochemical and electrochemical sensors,⁸ optoelectronic and microelectronic devices,⁹ and energy storage devices.¹⁰ Although graphene possesses remarkable properties, its widespread use has been hindered by difficulties in large-scale production and its limited reactivity due to the lack of functional groups on its surface.^{11,12} However, recent progress in the mass production of graphene and its derivatives, including graphene oxide (GO), reduced graphene oxide (rGO), and functionalized graphene nanosheets, has helped to overcome many of these challenges.^{13–15} Chemically modified and functionalized graphene has become a key focus of research in graphene-based materials, particularly for applications in supercapacitors.^{16–21} The growing interest in graphene functionalization stems from the potential to tailor its physical and chemical properties by adding specific organic groups to either the basal plane or the edges of graphene. Studies suggest that incorporating chemically reactive species, like amines,^{22,23} modifies the reactivity and chemistry of graphene's surface,





Graphene–MXene van der Waals heterostructures for high-performance supercapacitors

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ABSTRACT

Research on the exploration of graphene and two-dimensional (2D) materials is thriving and is anticipated to continue leading the forefront of materials science research. This growing interest in 2D nanomaterials is attributed to their distinct characteristics not present in their bulk counterparts. While various 2D nanomaterials have been developed, graphene and MXene, notably, have garnered significant global attention owing to their outstanding properties. Further, the ability to create van der Waals heterostructures has introduced a novel approach to amalgamating the advantageous features of graphene and MXene into a unified entity. These heterostructures not only overcome the inherent limitations of each material but also facilitate the realization of fascinating properties through their synergistic combination. This review discusses the evolution, recent advancements and prospects of these novel 2D materials. Additionally, we also address the challenges that must be overcome to achieve full-scale commercial adoption of this innovative class of layered materials. We also reviewed the application of graphene–MXene heterostructures for developing next-gen supercapacitor devices and outline potential directions for future research.

KEYWORDS

supercapacitors, graphene, MXene, van der Waals heterostructures, two-dimensional (2D) heterostructures

1 Introduction

The swift rise in the global human population has imposed a strain on energy security [1, 2]. The escalating combustion of fossil fuels underscores the critical need to integrate cleaner energy technologies into our daily lives. Hence, it is crucial not only to investigate cleaner and sustainable energy sources but also to advance the development of improved energy storage devices [3, 4]. This ensures that energy harvested from sources like the sun and wind can be effectively stored and utilized as per demand [5]. Thus, numerous energy storage devices have been developed in the last decades, including alkali-metal ion batteries (for instance, Li-ion batteries), and supercapacitors [6]. Technically, the performance of these energy storage systems is primarily determined by the properties and characteristics of the electrodes [7]. Until now, many novel materials such as sulfides, activated carbon, graphite, metal oxides, carbides have demonstrated captivating electrochemical performance when utilized as an electrode in energy storage devices [8]. Although these materials exhibit some of the necessary properties, none of them can provide all the required features essential for maximizing energy density (E_d), power density (P_d), and cycle life simultaneously [9].

In pursuit of advancing energy storage technologies, numerous studies have concentrated on exploring design and features principles of electrode materials. These include structural design, growth on substrates, and protective layer coating, all of which significantly improve pristine materials' performance [6]. A particularly compelling approach is the integration of materials into heterostructured architectures (Fig. 1(a)), which can be compared to assembling two-dimensional (2D) crystals like lego blocks, allowing for the construction of a wide variety of layered structures. These heterostructures combine the strengths of individual components while overcoming their limitations [9]. In the context of energy storage, this analogy is especially relevant, as the combination of different 2D materials in heterostructures lead to enhanced properties tailored to meet the specific demands of modern devices. Overall, heterostructures demonstrate superior performance compared to their individual building blocks, underscoring the potential of this approach.

The idea of heterostructure was first proposed by W. Shockley for semiconductor application [10, 11]. According to them, a heterostructure comprises different semiconductors characterized by similar atomic spacings, crystal structures, and coefficients of

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Evaluation of a novel activated carbon/graphene oxide as an efficient composite adsorbent for the removal of herbicide 2,4-Dichlorophenoxyacetic acid: Adsorption isotherm and kinetics study

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ABSTRACT

Thysanolaena maxima-derived activated carbon/graphene oxide (TMAC/GO) composite was synthesized through a one-step mixing process via ultrasonication and used as an adsorbent for the removal of 2,4-Dichlorophenoxyacetic acid (2,4-D) herbicide from solution. Various analytical techniques, including Fourier-transform infrared spectroscopy (FTIR), Field emission scanning electron microscopy-energy dispersive X-ray spectroscopy (FESEM-EDX), X-ray diffractometer (XRD), Brunauer, Emmett, and Teller (BET) surface area analyzer, and Transmission electron microscopy (TEM) were employed to characterize the synthesized composite. Results showed that the TMAC/GO had a porous structure with a large surface area of $960 \text{ m}^2/\text{g}$, an average pore diameter of 2.658 nm , and a total pore volume of $0.6372 \text{ cm}^3/\text{g}$. A series of batch experiments were conducted for different adsorption parameters, which include TMAC/GO dosage ($0.05\text{--}0.25 \text{ g/L}$), initial concentration ($50\text{--}300 \text{ mg/L}$), pH ($2\text{--}12$), contact time ($20\text{--}140 \text{ mins}$), and temperature ($298\text{--}398 \text{ K}$). Adsorption thermodynamics, isotherm models, and kinetics were employed to understand the adsorption mechanism. The composite showed good adsorption ability with the Langmuir maximum adsorption capacity of 98.469 mg/g . When compared with TMAC, the composite exhibited higher removal efficiency under the same dosage, concentration, and temperature with variations in pH and time. The pseudo-second-order kinetics model justified the experimental results with an R^2 value of 0.997 . Furthermore, the composite displayed good reusability performance up to 5 cycles. These findings, along with the cost-effectiveness of the material and its selectivity towards the herbicide, suggest its practical importance for water decontamination.

1. Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D) is widely used to manage broad-leaved weeds and pests in agricultural fields due to its cost-effectiveness and adequate selectivity [1]. Nevertheless, 2,4-D presents considerable environmental concerns as a pollutant, primarily because it degrades slowly in the environment [2]. 2,4-D is classified as a phenoxy compound; it is regarded as moderately toxic and falls into a category of chemicals that could pose risks to human health due to its carcinogenic and mutagenic properties [3]. The herbicide's maximum permissible concentration in potable water is 100 ppb (0.1 mg/L) [4]. The concentration decreased below 3.13 mg/L can result in an unpleasant taste and odour, failing to meet the standards established by the World Health Organization (WHO, 2003) [5]. Environmental exposure to this

herbicide, even in small amounts, can pose adverse health effects, particularly affecting vital organs in humans, such as the central nervous system, liver, and kidneys [6,7]. Besides that, the herbicide is associated with various reproductive health risks, including a higher incidence of abnormal sperm, sperm immobility, and sperm death, as well as an increase in lymphocyte levels and immune deficiency disorders. Studies on exposed animals have also reported fetal mortality, disorders of the urinary system, and congenital defects [8]. Furthermore, 2,4-D contributes to the degradation of soil and water resources because of its complex chemical composition, toxicity, and persistence in the environment [9]. Despite contamination risks, its use in agriculture will inevitably continue, adversely affecting water quality and human health [10]. Therefore, developing methods for the adsorption and removal of 2,4-D from soil, water, and wastewater is crucial for reducing

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Short communication



Preparation of Co-doped TiO₂ activated carbon nanocomposite and its photocatalytic degradation of phenol wastewater

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 Phenol
 Regeneration
 TiO₂-Activated Carbon nanocomposite

ABSTRACT

Co-doped TiO₂ supported on activated carbon (CT@AC) nanocomposite was prepared via a hydrothermal approach. The nanocomposite was characterized by various analytical methods like FT-IR, UV-vis DRS, SEM-EDX, photoluminescence (PL) and XRD. The visible light active nanocomposite was utilized for the degradation of phenol from an aqueous solution. The findings suggested that the introduction of Co²⁺ ions enhances the photocatalytic activity under visible light, enhances the surface area of the nanocomposite, decreases the bandgap energy, reduces recombination rate, and enhances the efficiency of transferring photogenerated electrons. The degradation efficiency with 0.35 g of the Co-doped TiO₂/Activated carbon nanocomposite was found to have a catalytic rate of ~100 % for 20 mgL⁻¹ phenol solution.

1. Introduction

In recent years, contamination of water resources due to rapid industrial development and modernization has stimulated significant concern worldwide [1]. Of various contamination, phenols are one of the contaminant that are frequently discharged as waste products from the pharmaceutical industries, plastic plants, oil refineries, textile industries, and coal conversion industries [2]. Phenols are found to be bioaccumulative, persistence, widespread, and poor biodegradability which makes it a contaminant of concern to the environment. Upon ingestion of phenol, different health-related problems could arise such as metabolic acidosis, respiratory distress, renal failure, cardiovascular effects, neurological effects, necrosis of the skin, gastrointestinal irritation, abdominal pain, and paralysis [3]. Phenol retains its toxicity effects in our body even at a concentration lower than 10 ngL⁻¹ [4]. Hence, the removal of phenol from water sources has become a major challenge for the scientific community. At present, several methods are applied to remove phenols from wastewater viz., nanofiltration [5], adsorption [6], Fenton [7], electrodialysis [8], ion exchange [9], reverse osmosis [10], electrochemical degradation [11], membrane filtration [12], electrocoagulation [13], wet oxidation [14] and phytoremediation [15]. Although these methods successfully remove phenol from wastewater, there are some concerns related to secondary waste generation,

operation difficulty, reliability, pre-treatment requirements, environmental impact and formation of toxic by-products [16]. In this context, advanced oxidation processes (AOPs) are getting attention due to their ability to degrade non-biodegradable pollutants in addition to their high treatment potential [17–20]. In AOPs, upon exposure of light of a particular wavelength onto a photocatalyst, highly photo-reactive hydroxyl radicals (•OH) are generated. The reactive radicals perform a redox reaction with the electron-hole pairs of the photocatalyst and further degrade pollutant compounds to CO₂ and H₂O [21,22]. For instance, Rajeshwari et al [23], investigated the use of a novel g-C₃N₄ quantum dots incorporated into an α-MoO₃ nanohybrid for degradation of p-chlorophenol and rifampicin using visible light. Till date, numerous types of photocatalysts have been used such as TiO₂, Bi₂O₃, SnO₂, Fe₂O₃, WO₃, and g-C₃N₄ [23–25]. TiO₂ among them, in its anatase phase has garnered much attention owing to its unique properties such as photochemical stability, non-toxicity, biological and chemical inactivity, and environmental-friendly nature [26]. However, high recombination between electron-hole pairs impedes their applicability in the visible light region [27].

Therefore, various strategies such as metal/non-metal doping [28–30], hydrogen treatment [31], and photosensitization using dyes [32] have been employed to improve the visible light-induced photocatalytic activity of TiO₂. Among these alternatives, introduction of transition

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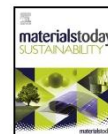
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2D transition metal dichalcogenides for efficient hydrogen generation

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ABSTRACT

The transition towards renewable energy sources is imperative as conventional fossil fuels are being depleted and have harmful impact on the environment and human life. Hydrogen (H₂) has become a favorable energy carrier because of its significant energy density. Green production methods such as electrochemical water splitting shows promise as a low cost and environmentally benign approach for H₂ generation. Lately, the progress in 2D transition metal chalcogenides (TMDs) nanomaterials with diverse physicochemical features has demonstrated their promise as prominent non-noble metal-based electrocatalysts for hydrogen evolution reaction (HER). This review explores recent advancements in TMD-based electrocatalysts for HER, highlighting the mechanisms of HER, parameters for evaluation of electrochemical water splitting, strategies for enhancing performance, and future research directions. Through a comprehensive examination of recent literature, this review provides insights into the potential of TMDs in advancing renewable energy technologies and the development of highly efficient catalyst towards HER.

1. Introduction

The widespread use of traditional fossil fuels such as coal, oil, and natural gas have resulted in their rapid depletion. The dependency on non-renewable energy sources not only harm our environment, but also negatively impacts the human life [1–3]. Currently, world is running towards renewable energy sources, including wave, tidal, and solar. Though renewable energy offers obvious positives, the notion may even be detrimental to efforts to address climatic conditions. This is due to the uneven geographic distribution which contribute to their irregular availability [4,5]. At the moment, renewable energy represents a tiny percentage, only 14% of total global energy demands, despite various attempts by countries worldwide [6]. Fig. 1 depicts the global distribution of renewable energy capacity (2018–2050) around the globe [7].

Among the plethora of energy sources, H₂ stands out as a superior energy carrier, primarily owing to exceptional energy density (142 MJ/kg⁻¹), abundant sources, high efficiency, sustainability and environment friendly nature [2,3,8–11]. It is the lightest and readily available element on earth and is derived from different sources (both renewable and non-renewable) using different pathways and technologies [5,12]. H₂ can be classified into four distinct types: grey, blue, turquoise, and green hydrogen according to the production method, the energy source employed, and the environmental impact [13,14]. Grey

hydrogen refers to H₂ generated through coal gasification or steam reforming of natural gas without incorporating CO₂ capture, storage and utilization technologies. On the other hand, H₂ produced via steam methane reforming, using natural gas or biomass, with the implementation of CO₂ capture, storage and utilization technologies is termed as blue hydrogen. Turquoise hydrogen is derived through the pyrolysis of fossil fuels, resulting in solid carbon as a by-product [15–18]. In contrast, H₂ produced through water electrolysis, known as green hydrogen, offers a sustainable solution by emitting zero carbon byproducts. Thus, water electrolysis is a viable and environmentally benign way of energy production that reduces the dependency on finite fossil fuel and mitigates severe global climate change [2,19]. Production of H₂ in large-scale from electrochemical water splitting depends on the effective catalyst employed in HER [1]. At present, the platinum-group elements like Pt, Rh, Pd and Ir serve as the most efficient catalysts, exhibiting very low overpotential (η) for HER [8,9]. However, their high cost, poor durability and finite supply constrain their widespread applications [8,20,21]. Therefore, researchers are exploring earth-abundant materials as alternatives that could fulfill the roles of precious metal-based electrocatalysts. In recent times, there has been notable focus towards catalysts based on transition metal including carbides [22], nitrides [23], borides [24], phosphides [25], layered double hydroxides (LDHs) [26] and TMDs [27]. Of these materials,

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Experimental and DFT study on the removal of sulfadiazine by activated carbon prepared from *Rubus alceifolius*

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Abstract

This study describes the synthesis of activated carbon from locally derived biomass *Rubus alceifolius* using ZnCl_2 as an activating agent for sulfadiazine (SDZ) removal from wastewater. The adsorbent material was characterized by Fourier transform infrared (FTIR), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), N_2 adsorption–desorption isotherms, and zero-point charge (pH_{zpc}). Brunauer–Emmett–Teller (BET) surface area and total pore volume of the synthesized carbon were found to be $233 \text{ m}^2 \text{ g}^{-1}$ and $0.16 \text{ cm}^3 \text{ g}^{-1}$, respectively. Batch adsorption studies were carried out under varying initial concentrations, adsorbent dosage, temperature, contact time, and pH to comprehend the effects of different operating parameters on the removal efficiency for sulfadiazine from wastewater. The equilibrium isotherm study fitted well with the Langmuir model with maximum adsorption capacity (q_m) of 29.57 mg g^{-1} . The adsorption kinetic was best fitted by the pseudo-second-order model. Thermodynamic process of adsorption of SDZ onto activated carbon was found to be spontaneous and endothermic. Theoretical investigations using density functional theory (DFT) calculations suggested that the adsorption of SDZ onto functionalized activated carbon is favorable. Among the oxygen-containing functional groups, the carboxyl group appeared to have the largest effect on the adsorption process. However, DFT calculation showed that the presence of all three oxygen-containing functional groups enhanced the adsorption of SDZ, compared with pristine activated carbon.

Keywords *Rubus alceifolius* · Activated carbon · Adsorption · Sulfadiazine · Density functional theory

Abbreviations

RAAC	<i>Rubus alceifolius</i> activated carbon
SDZ	Sulfadiazine
DFT	Density functional theory
pH_{zpc}	Zero-point charge
AC	Activated carbon
AC_P	Pristine AC
AC_COOH	COOH functionalized AC
AC_OH	–OH functionalized AC
AC_CHO	–CHO functionalized AC
OH+CHO+COOH_AC	–OH, –COOH, –CHO functionalized AC

1 Introduction

Antibiotics are drugs that are commonly used as a preventative and therapeutic treatment for infections caused by microorganisms, by obstructing their metabolism via biochemical activities [1]. Due to the rapid increase in antibiotic use around the world, they are often found in urban wastewater, surface water, groundwater, and drinking water. This is a growing concern as antibiotic residue may give rise to the emergence of antibiotic-resistant microorganisms in marine environments [2, 3]. Antibiotics are divided into several classes, including nitroimidazoles, sulfonamides, tetracyclines, chloramphenicol, quinolones, and fluoroquinolones. Sulfadiazine belongs to the class of antibiotics called sulfonamides, and they are frequently used in aquaculture and animal husbandry [4]. Probably due to its high consumption and affordable cost which leads to its high consumption, it has been reported that SDZ has been detected at high concentrations in sewage treatment plants [5]. Consequently, SDZ antibiotics have garnered global attention for their negative role in

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Utilization of *Pinus kesiya* and *Schima wallichii* Biomass-Derived Activated Carbon for Methylene Blue Removal: Adsorption Performance and Mechanistic Insights

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Abstract

Biomass material offers several advantages to synthesize activated carbon because of its economic viability, renewability, availability, and unique physicochemical properties. This piece of work reports activated carbon prepared from biomass of *Pinus kesiya* and *Schima wallichii* via ZnCl_2 activation for potential application to remove methylene blue from water. The optimum adsorption parameters—pH, adsorbent dose, and agitation speed—were obtained using Taguchi design of experiment. Experimental equilibrium data of adsorption of methylene blue onto the adsorbents fitted well with Langmuir isotherm with maximum adsorption capacity of 116.28 mg g^{-1} and 95.24 mg g^{-1} for *Pinus kesiya* activated carbon and *Schima wallichii* activated carbon respectively. The kinetic experimental data followed a pseudo-second-order equation for both the adsorbents. The potential rate-controlling step in the adsorption of methylene blue onto the adsorbents was predominantly intraparticle diffusion with two stages of adsorption for *Pinus kesiya* activated carbon and three stages of adsorption for *Schima wallichii* activated carbon. Density functional study investigation suggested that methylene blue adsorption onto activated carbon is predominantly chemisorption, and the presence of a carboxylic acid functional group on the activated carbon surface has a higher methylene blue adsorption affinity with an adsorption energy of $-171.85 \text{ kJ mol}^{-1}$ compared to $-\text{CHO}$ and $-\text{OH}$ functionalized carbon, pristine activated carbon models. Our work indicates that activated carbon derived from *Pinus kesiya* and *Schima wallichii* biomass could be an efficient adsorbent to remove methylene blue from water.

Keywords Activated carbon · Methylene blue · Biomass · Adsorption

Introduction

Water represents life and is the heart of sustainable development. But the current state of the water is not in its pristine state and is polluted with various undesirable substances. Pollution of water from myriad sources, both natural and anthropogenic poses a significant threat to human and

animal health, and the environment. Substances, such as dyes, are of urgent concern because of their recalcitrance nature, photochemical stability, and for giving undesirable color even at significantly low concentrations [1]. Furthermore, degraded products often have mutagenic and carcinogenic health risks [2]. It even accelerates the chemical and biological oxygen demand levels in aquatic bodies, which hampers the natural aquatic ecosystem [1]. Synthetic dyes are substances widely used in industries—paper, textile, leather, pulp, printing, food, and plastic—from where they enter the water bodies and often pollute them. With urbanization and industrialization, the amount of wastewater has increased, which must be treated before use. Moreover, it is reported by various researchers that more than 100,000 commercial dyes are available, and dyes being tinctorial are visible even in trace quantity [3].

Methylene blue (MB) has been extensively investigated among various dyes because of its strong adsorption ability onto solid surfaces. MB is also often used as a model

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Photocatalytic degradation of the organophosphorus insecticide chlorpyrifos in aqueous suspensions using a novel activated carbon ZrO₂-ZnO nanocomposite under UV light

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Abstract—This paper describes the photocatalytic degradation of the organophosphorus insecticide chlorpyrifos in aqueous suspensions using *Schima wallichii* activated carbon/ZrO₂-ZnO (SWAC/ZrO₂-ZnO) nanocomposite in UV light. Analytical techniques such as XRD, FT-IR, TEM-SEAD, XPS, PL, and BET analyzer were used to characterize the SWAC/ZrO₂-ZnO nanocomposite. The BET surface area of the photocatalyst was found to be 223.387 m²g⁻¹, having a total pore volume of 0.1845 cm³g⁻¹. The photocatalytic degradation of chlorpyrifos followed pseudo-first-order rate kinetics with a half-life period ($t_{1/2}$) of 7.088 mins and K_p (apparent rate constant) of 0.09778 min⁻¹. The mechanism of composite formation was explained using DFT investigations, which demonstrated a favorable immobilization of ZrO₂-ZnO on SWAC. Chemical descriptors gained from DFT investigations, such as HOMO-LUMO energy, ionization energy, dipole moment, chemical softness, and chemical hardness, supported an understanding of the relative efficiency and reactivity of ZrO₂-ZnO and SWAC/ZrO₂-ZnO towards chlorpyrifos degradation.

Keywords: SWAC/ZrO₂-ZnO Nanocomposite, Photocatalytic Degradation, UV Light Irradiation, Kinetics

INTRODUCTION

Pesticides are designed to control pests; however, their widespread use in industrial and agricultural activities has become a matter of concern as the discharges from these sources contaminate water systems. Chlorpyrifos (CPs) is a common organophosphate insecticide used in agriculture to boost production and protect crops from insects and pests. The presence of chlorpyrifos in water can cause skin irritation, headaches, nausea, respiratory failure, stomach cramps, and even death in humans [1,2]. Therefore, developing a new and efficient method of wastewater treatment is necessary to remove organic pollutants from the aqueous medium. Several novel approaches for chlorpyrifos-containing wastewater treatment have been suggested to date. These involve the application of electrochemical degradation [3], ionizing radiation [4], biodegradation [5] batch adsorption [6], and photocatalytic degradation [7]. Out of various approaches, the development of the photocatalytic technique is one of the most potential processes for the degradation of organic contaminants due to its ease of use, high efficiency, lack of secondary pollution, and low cost [8]. This method takes place in the presence of light wherein the semiconductor materials absorb the energy of a photon $\geq E_g$ (bandgap) and promotes an electron from the valence band to the conduction band. This allows for the creation of an electron in the conduction band and a positive hole in the valence band. Thus, the electron behaves as a reductant and the positive hole as an oxidant in the photocatalytic method [9].

Some of the metal oxide nanoparticle photocatalysts employed

for the degradation or removal of organic compounds in aqueous media are ZnS (Zinc sulfide), TiO₂ (Titanium dioxide), ZnO (Zinc oxide), WO₃ (Tungsten trioxide), CuO (Copper oxide), and ZrO₂ (Zirconium dioxide) [10,11]. Under UV radiation, these metal oxides degrade organic compounds, transforming them into harmless end products through various steps. Out of these, ZnO has been extensively studied because of its superior photocatalytic activity, stability, non-toxicity, and low cost [12]. However, ZnO has disadvantages such as photocorrosion and instability when exposed to light. Furthermore, a high recombination rate of photogenerated holes and electrons renders the photocatalytic process ineffective [13]. As a result, ongoing attempts are being made to increase the photocatalytic activity of ZnO by coupling or doping with metal/metal oxides. The well-known metal oxide zirconium dioxide (ZrO₂) has high thermal stability, excellent corrosion resistance, a high dielectric constant, and a wide band gap energy of ~5.0 eV [14]. Although the ZrO₂ band gap value is insufficient for degradation studies, its monoclinic phase and composite form help to improve the photocatalytic activity. Further presence of ZrO₂ in ZnO/ZrO₂ complexes increases the generation of *OH radicals, which is also responsible for the increase in photoactivity. Therefore, the presence of ZrO₂ can strengthen the thermo-mechanical and chemical stability of ZnO. Simultaneously, the presence of ZnO can reduce the band gap of ZrO₂ [15]. In addition, ZnO undergoes dissolution at lower pH, but when coupled with ZrO₂ it can improve the dissolution resistance at lower pH as reported [16].

Numerous researchers have concluded that incorporating an adsorbent and a photocatalyst system improves the removal percentage of organic pollutants [17-19]. Activated carbon (AC) is a type of co-adsorbent widely utilized as key support for the photocatalyst in the treatment of wastewater through photocatalytic deg-

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Activated carbon adsorbent derived from waste biomass, “*Croton caudatus*” for efficient removal of 2-chlorophenol from aqueous solution: Kinetics, isotherm, thermodynamics and DFT simulation

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ABSTRACT

The present study aims to prepare an activated carbon (AC) adsorbent developed from *Croton caudatus* biomass material for the adsorption of 2-chlorophenol (2CP) from wastewater. Activated carbon was prepared by KOH activation at 2:1 impregnation ratio and 700 °C temperature using a muffle furnace under self-generated atmosphere for 2 h. Several techniques and methodologies such as proximate analysis, ultimate (CHNS) analysis, BET, SEM, FT-IR, XRD and point of zero charge (pH_{pzc}) have been used to determine physicochemical properties of the activated carbon. Batch adsorption studies were conducted for 2-chlorophenol adsorption and the optimum adsorbent dose, initial concentration, pH, reaction time and temperature were found to be 0.15 g/L, 80 mg/L, 4, 60 min and 298 K, respectively. The equilibrium isotherm study for 2-chlorophenol adsorption was fitted well to the Langmuir model with the adsorption capacity of 53.619 mg/g, while the adsorption kinetics was best described by pseudo-second order model. Thermodynamic parameters demonstrated a negative ΔH (exothermic) and negative ΔG (spontaneous) values. Studies on regeneration have shown that saturated carbon can be recycled up to five times with considerable removal efficiency. Besides, density functional theory (DFT) simulation revealed that the adsorption of 2-chlorophenol onto AC adsorbent is favorable. Among the oxygen-containing functional groups, the carboxyl group appeared to have a greater influence on the adsorption process than the hydroxyl and carbonyl groups with the highest negative $E_{adsorption}$ of -42.16 kJ/mol. Furthermore, the inclusion of three oxygen-containing functional groups improves the adsorption capacity of AC towards 2CP relative to a single functional group.

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Abbreviations: CCAC, *Croton caudatus* activated carbon; CP, chlorophenol; EPA, environmental protection agency; DFT, density functional theory; wt%, weight percentage; RMSE, Residual root mean error; AC, activated carbon; p-AC, pristine activated carbon; COOHAC, carboxyl functionalized activated carbon, OH(AC), hydroxyl functionalized activated carbon; CHOAC, carbonyl functionalized activated carbon; OH+CHO+COOHAC, hydroxyl, carboxyl and carbonyl functionalized activated carbon; pH_{pzc} , zero-point charge

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Synthesis, characterization of novel Fe-doped TiO₂ activated carbon nanocomposite towards photocatalytic degradation of Congo red, *E. coli*, and *S. aureus*

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Abstract—In this work, the synthesis, characterization, and photocatalytic activity of iron-doped titanium dioxide nanoparticles (FDT) supported on environmentally benign activated carbon (PAC) has been discussed. The photocatalytic activity of the nanocomposite was investigated for the degradation of Congo red (CR) dye from aqueous solution under visible light (520 nm), and it was observed that 100% degradation for 20 ppm CR solution took place within 60 mins. The experimental data of photodegradation of CR using the FDT/PAC nanocomposite had the highest correlation with Langmuir-Hinshelwood model and pseudo-first-order rate kinetics with an apparent rate constant of 0.05341 min⁻¹ and half-life period of 12.97 mins, respectively. The thermodynamics study revealed that the degradation process is exothermic and spontaneous. The effect of interfering ions on the degradation of CR solution was also examined. The photocatalytic antibacterial activity of the nanocomposite was tested against two bacteria pathogens, *Escherichia coli* and *Staphylococcus aureus*, and it was found that for the concentration of 10⁷ CFU ml⁻¹, 100% photocatalytic inactivation was achieved for both *Escherichia coli* in 120 mins and *Staphylococcus aureus* in 75 mins under visible light irradiation. The total electrical energy consumed and operating cost were measured and the total operating cost was 312.50, 236.74, and 166.67 INR (Indian rupee) for 20 ppm, 60 ppm, and 100 ppm CR dye removal using 0.06 g FDT/PAC nanocomposite, respectively.

Keywords: FDT/PAC Nanocomposite, Photodegradation, Congo Red Dye, Antibacterial Activity, Electric Energy Per Order

INTRODUCTION

The impact of nanotechnology has become increasingly evident in different areas of science and technology, including environmental remediation and disinfection. Several environmentally beneficial technologies, such as heterogeneous photocatalysis (HP) and solar disinfection (SODIS) using metal oxide semiconductor photocatalysts, have been developed and applied extensively for air purification, wastewater treatment, and environmental regulations [1-3]. Among all the metal oxides used, TiO₂ is the most potential photocatalyst due to its chemical constancy, low cost, less harm, photochemical stability, and no further requirement of secondary disposal and expensive oxidizing chemicals. However, a high recombination rate between electron and hole pairs limits the use of TiO₂ in the visible region (400-750 nm), which accounts for 43% of solar light [4]. Therefore, to overcome this problem, it is desired to alter the band structure of the anatase TiO₂ and, in this regard, different methodologies like metal/non-metal elements doping, dye photosensitization, hydrogen treatment have been developed to enhance the TiO₂ photoactivity in the visible light region [4]. Among different alterations, transition metal doping is a simple and efficient approach to widen the wavelength region of TiO₂ to the visible light

range [5]. The use of dopant in the metal oxide creates an intermediate level in the lattice which constrains the electron-hole pair to recombine, and hence the recombination rate decreases and ultimately the photocatalytic activity of TiO₂ gets enhanced [6]. Among the different metal dopants, Fe³⁺ has garnered more attention due to its ionic radius of 0.64 Å, which is identical to the ionic radius of Ti⁴⁺ (0.68 Å); therefore, making it easier to substitute Fe³⁺ into the crystal structure of TiO₂. Application of Fe doped in TiO₂ has been widely reported for the degradation of environmental pollutants [7-9], NO_x removal [4], CO₂ reduction [10], and water splitting for hydrogen production [11]. Literature reports have showed that the incorporation of Fe³⁺ ions in the TiO₂ lattice reduces the electron-hole recombination rate, narrows the TiO₂ band gap, and thus increases the photocatalytic activity of TiO₂. However, powdered TiO₂ has low exchange efficacy and is difficult to split after the photocatalytic reaction [7]. Hence to achieve quick and easy degradation of organic pollutants and also for simple management of the photocatalyst, it is desired that TiO₂ be loaded onto an appropriate adsorbent. In this regard, different adsorbents such as zeolites, perlite, clay, silica, and activated carbon have been used as support systems for TiO₂ [12]. Activated carbon with good adsorption capacity is more appropriate as an adsorbent support system for the photocatalyst in any wastewater treatment process, as it can significantly gather pollutant molecules near the photocatalytic sites during the adsorption-degradation process. Additionally, the synergistic effect between activated carbon and TiO₂ will separate the

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DFT study on the structural, optical and electronic properties of platinum group doped graphene

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ABSTRACT

The present study attempts to explore the effects of doping graphene with platinum group elements (PGE), i.e., ruthenium, rhodium, palladium, osmium, iridium, and platinum. The variation in the structural, optical and electronic properties of the doped systems have been studied through density functional theory. Gaussian 09 suite of the program was used at B3PW91/LANL2DZ level of theory for optimizing the structures to their lowest energy states and evaluating various molecular descriptors i.e., formation energy and stability, HOMO-LUMO energy gap, density of states (DOS), UV-vis absorption spectra, and Mulliken population analysis. Interpretation of the above parameters revealed that the doping of graphene with the PGE is likely to enhance the structural, optical and electronic properties of the same; which can thereby be utilized in designing novel materials for different applications like wearable electronics, optoelectronics, sensors, solar cells, etc.

1. Introduction

Since the past few decades, there has been a surge in the use and application of nanomaterials across the globe [1–7]. Their fascinating properties make them extensively employable in numerous fields of science and technology such as drug delivery systems, tissue engineering, treatment of cardiovascular and neurological diseases, paints, cleaning products, cosmetics, filtration, sensors etc. [8–13]. Among the various classes of nanomaterials, carbon-based nanomaterials such as carbon nano tubes (CNTs), activated carbon (AC), fullerenes etc., have attracted wide attention due to their efficiency and diverse applications [14–23]. In recent times, another allotrope of carbon, graphene has captured the fascination of the scientific community because of its exceptional set of properties [24–31]. Graphene is a 2D array of sp^2 hybridised carbon atoms arranged in a hexagonal honeycomb lattice to form a flat monolayer of carbon atoms [24,32,33]. Geim and Novoselov were the first to isolate it in 2004 [34] and it is the basic building block of other graphitic materials of all other dimensionalities such as fullerenes, nanotubes, graphite. The graphene sheets can be wrapped up to form 0D fullerenes, rolled to form 1D nanotubes or stacked on top of each other to form the 3D graphite. In other words, it can be considered as the “Mother of all graphitic forms” [24]. It exhibits unique properties such as high specific surface area, high conductivity [24], excellent optical, electronic [29], thermal and mechanical [30,31] properties etc.

These inimitable and alluring properties of graphene makes it a potent material candidate in a wide array of fields such as catalysis [35,36], sensors [37,38], energy storage [39–41], water purification [42,43], optoelectronics [44] as well as in many other applications [24,34,45–47].

Despite these favourable properties, there are many challenges that restrict the use of graphene in manufacturing devices [48], thereby causing immense need to tailor the properties of graphene as per the needs and requirements for its use in diverse applications. In this regard a substantial amount of work has been done to fine tune graphene's properties [49–55]. Recently, the method of doping has drawn much attention as it is one of the simplest and effective ways to alter and modulate the properties of graphene, which can be achieved by regulating the degree of doping and/or doping with different hetero atoms [56]. It is found that the electronic properties of graphene like charge distribution, density of states, energy levels etc., change considerably when doped with heteroatoms such as N, B, O etc. [35,50,53,56–59], possibly due to the electronegativity difference between carbon atom and the dopants. Although, doping with various heteroatoms have been extensively studied, there are limited reports about doping with platinum group elements (PGE) and its effects on the structural, optical and electronic properties of graphene [60–64]. PGE consists of ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt), and has a number of desirable properties such as high

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Electrochemical Diagnostics in Water Splitting: Methods and Best Practices



Suraj Kumar, Priyakshi Bora, and Dipak Sinha

Abstract Electrochemical water splitting offers an efficient pathway for hydrogen generation, playing a key role in advancing green energy solutions. While developing efficient electrocatalysts is crucial, ensuring accurate evaluation of their performance is equally important. However, the rapid expansion of materials science and the growing interdisciplinary interest in electrochemistry have led to widespread misinterpretation of data, particularly among beginners to the field. This chapter lays out essential guidelines for assessing water-splitting electrocatalysts. It covers critical factors like experimental setup, electrode selection (reference, counter and working), and electrolytes. Additionally, it outlines key metrics for evaluating catalytic activity, selectivity, and stability, along with recommendations and best practices for standardized data reporting to enhance clarity and reproducibility in the field.

1 Introduction

Electrochemical water splitting, when driven by green energy, is a highly efficient technique for the large-scale production of green hydrogen. The procedure encompasses two principal half-reactions: the hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode (Fig. 1a) [1]. The HER is a relatively simple process including a series of adsorption, discharge, and desorption reactions involving protons or water molecules to generate hydrogen gas. Conversely, the OER is a multi-step, complex reaction that entails the formation of several intermediates including the reduction and self-oxidation of electrocatalysts [2]. Despite its promise, water splitting faces significant kinetic limitations, particularly for the OER, which requires considerable overpotentials (η) to proceed efficiently. Addressing these issues requires the design of efficient, cost-effective, earth-abundant and durable electrocatalysts that can achieve high current densities while operating at low overpotentials [2, 3]. Some researchers employ systematic computational and experimental

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LIST OF PATENTS

S.No.	Patent Title	Name of Applicant(s)	Patent No./ Application No.	Award Date/ Date of filing	Country/ Status
1.	Synthesis of Bromographene for High-Performance Supercapacitors with Enhanced Energy Density	Suraj Kumar , Priyakshi Bora, Basanta Singha, Dipak Sinha and Upasana Bora Sinha	2025310316 88 A	31/03/2025	India (Published)
2.	A process for synthesizing aminated reduced graphene oxide and a composition for the same	Suraj Kumar , Dinesh Rangappa, Priyakshi Bora, Navya Rani M, Dipak Sinha	563060	20/03/2025	India (Granted)
3.	System zur Synthese und Charakterisierung von aus Rubus Alceifolius hergestellter Aktivkohle zur Entfernung von Sulfadiazin	Raplang Steven Umdor, Shisak Sharma, Dipak Sinha, Suraj Kumar , Imotila Longchar	20 2024 103 104	27/06/2024	Germany (Granted)
4.	Ein System zur umweltfreundlic	Suraj Kumar , Dinesh	20 2024 101 833	22/04/2024	Germany (Granted)

	hen und schnellen Synthese von Bromographen (BG) unter Verwendung eines umweltfreundlic heren Bromierreagenz	Rangappa, Basanta Singha, Dipak Sinha, Upasana Bora Sinha, Aola Supong			
5.	A process of preparation of Fe- Doped ZnO/activated carbon nanocomposite for photocatalytic degradation of chlorpyrifos	Soremo L Ezung, Mridushmita Baruah, Suraj Kumar , Shisak Sharma, Raplant Steven Umdor, Bupesh Giridharan, Dipak Sinha	2023310848 22 A	12/12/2023	India (Published)
6.	A process for the synthesis of antibacterial activity exhibiting brominated activated carbon and product thereof	Aola Supong, Parimal Chandra Bhomick, Suraj Kumar , Shisak Sharma, Dipak Sinha, Upasana Bora Sinha	571740	09/10/2025	India (Granted)

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(51) International classification :C01B32/184 (86) International Application No :NA Filing Date :NA (87) International Publication No :NA (61) Patent of Addition to Application Number :NA Filing Date :NA (62) Divisional to Application Number :NA Filing Date :NA		(71)Name of Applicant : 1)Nagaland University Address of Applicant :Nagaland University, Lumami Headquarters, Zunheboto district -India-798627 Zunheboto ----- Name of Applicant : NA Address of Applicant : NA (72)Name of Inventor : 1)Mr. Suraj Kumar Address of Applicant :Room No. 19 Kamnoi Hostel Nagaland University, Lumami Headquarters, Zunheboto district Zunheboto ----- 2)Priyakshi Bora Address of Applicant :House No. 62 Nagaland University, Lumami Headquarters, Zunheboto district Zunheboto ----- 3)Basanta Singha Address of Applicant :Room No. 14 Kamnoi Hostel Nagaland University, Lumami Headquarters, Zunheboto district Zunheboto ----- 4)Dipak Sinha Address of Applicant :Room No. 101 Kinimi Apartment Nagaland University, Lumami Headquarters, Zunheboto district Zunheboto ----- 5)Upasana Bora Sinha Address of Applicant :Room No. 101 Kinimi Apartment Nagaland University, Lumami Headquarters, Zunheboto district Zunheboto -----
(57) Abstract : The invention comprises a more environmentally friendly brominating agent, bromographene is created by effectively brominating reduced graphene oxide (rGO) with a tribromide through reflux for just one hour, which is the shortest time for rGO bromination that has been documented. By using this technique, bromination can take place in mild environments without the need for high pressure or temperature. By varying the concentrations of tribromide and rGO, the bromine content varied between 0.43 and 4.73%. For characterization, FTIR, XPS, XRD, and FE-SEM are used. The electrochemical characteristics are remarkable, exhibiting a broad potential window of 2.3 V and a specific capacitance of up to 826 F g ⁻¹ . A symmetric supercapacitor that used bromographene achieved 254 F g ⁻¹ , which is about 250% better than rGO. [To be published with figure 1]		
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über die Eintragung des
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Bezeichnung:

System zur Synthese und Charakterisierung von aus *Rubus Alceifolius*
hergestellter Aktivkohle zur Entfernung von Sulfadiazin

IPC:

B01L 99/00

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Sharma, Shisak, Zunheboto, Nagaland, IN
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Die Präsidentin des Deutschen Patent- und Markenamts



Eva Schewior

München, 27.06.2024



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Den aktuellen Rechtsstand und Schutzzumfang entnehmen Sie bitte dem DPMAregister unter www.dpma.de.

 Bundesrepublik Deutschland 

Urkunde

über die Eintragung des
Gebrauchsmusters Nr. 20 2024 101 833

Bezeichnung:

Ein System zur umweltfreundlichen und schnellen Synthese von Bromographen
(BG) unter Verwendung eines umweltfreundlicheren Bromierreagenz

IPC:

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Inhaber/Inhaberin:

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Rangappa, Dinesh, Chikkaballapur, Karnataka, IN
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(57) Abstract :
 TITLE: A PROCESS OF PREPARATION OF Fe-DOPED ZnO/ACTIVATED CARBON NANOCOMPOSITE FOR PHOTOCATALYTIC DEGRADATION OF CHLORPYRIFOS APPLICANT: NAGALAND UNIVERSITY ABSTRACT The present invention relates to a process of photocatalytic degradation of Chlorpyrifos in wastewater using Fe-doped ZnO/Activated Carbon Nanocomposite. The process of the present invention comprises of following steps; a. preparation of Schima wallichii activated carbon; b. preparation of SWAC/Fe-ZnO nanocomposite; Characterized in c. photocatalytic degradation of chlorpyrifos in waste water.

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