

Effect of Graphene Oxide Concentration and Sintering Conditions on the Electrical Conductivity of MnO₂/N-Doped Graphene Composites for Potential Lithium-Ion Battery Anode Applications

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Abstract

Advancing energy storage technology is crucial for a sustainable future. The development of sustainable anode materials is essential for advancing lithium-ion battery (LiB) technology. This study reports the synthesis, optimization, and characterization of a MnO₂/N-doped graphene (MnO₂/NDG) composite derived from puspa wood biomass via a one-step hydrothermal method. Variations in graphene oxide (GO) concentration (0.167, 0.25, and 0.5 mg/mL) and sintering temperature (400 - 550 °C) were conducted to optimize the composite's electrical conductivity. The materials were characterized using XRD, FTIR, UV-Vis, and TEM to identify crystal structure, functional groups, optical properties, and morphology. Results show that the optimum conditions were achieved at a GO concentration of 0.167 mg/mL and a sintering temperature of 550 °C, yielding a significantly enhanced electrical conductivity of 3.38×10^{-5} S/cm. This enhancement, stemming from the formation of a stable conductive network, addresses a key limitation for electrode applications. XRD and TEM analyses confirmed the formation of the α -MnO₂ (hollandite) phase with a nanorod morphology uniformly dispersed on graphene sheets. The sintering process strengthened Mn-O bonds and enhanced the reduction of GO to reduced graphene oxide (rGO), resulting in a stable conductive network. This study demonstrates the potential of puspa wood biomass as a sustainable carbon precursor for developing MnO₂/NDG composites with enhanced electrical properties for further investigation as anode materials.

Keywords: MnO₂/N-doped graphene, Puspa wood biomass, Lithium-ion battery, Anode material, Hydrothermal, Electrical conductivity

Introduction

The global shift toward sustainable energy systems requires efficient, reliable, and cost-effective energy storage technologies [1,2]. Lithium-ion batteries (LIBs) are widely used in applications ranging from portable electronics to grid-scale battery energy storage systems (BESS) due to their high energy density and long cycle life. However, the performance of current LIBs is limited by conventional graphite anodes, which have a relatively low theoretical capacity of 372 mAh g⁻¹ and suffer from slow reaction kinetics and poor performance at low temperatures [3,4].

To overcome these limitations, significant research has been directed towards high-capacity alternative anode materials [5,6]. Among them, conversion-type transition-metal oxides, particularly manganese dioxide (MnO₂), are highly attractive due to their high theoretical capacity ($\sim 1,232$ mAh g⁻¹), natural abundance, and environmental friendliness. MnO₂ functions as an effective anode material due to its unique layered crystal structure, which facilitates strong electrical bonding with lithium ions, thereby enhancing capacity and cyclability [7]. MnO₂ also has good chemical stability and corrosion resistance, which helps

improve battery reliability. Nevertheless, the practical deployment of MnO_2 anodes is limited by their intrinsically low electrical conductivity and severe volume expansion during lithiation/delithiation cycles, leading to rapid capacity decay and poor rate capability [8].

A proven strategy to mitigate these drawbacks is to incorporate MnO_2 into a conductive carbon matrix. Graphene, with its exceptional electrical conductivity, mechanical strength, and high surface area, serves as an ideal scaffold [9,10]. The performance of graphene can be further enhanced through nitrogen (N) doping. The introduction of nitrogen atoms into the graphene lattice creates microporous structures that improve electrode/electrolyte wettability and increases the binding energy for lithium ions, promoting greater ion mobility across the electrode surface. The higher electronegativity of nitrogen relative to carbon induces polarisation within the carbon network, thereby favourably altering graphene's electronic, magnetic, and optical properties and increasing its electrochemical activity. Consequently, N-doped graphene (NDG) has been widely reported in the literature to exhibit a higher capacitance and lithium storage capacity than its pristine counterpart [11,12].

Combining MnO_2 with NDG graphene yields a synergistic composite that harnesses the high capacity of MnO_2 and NDG's superior conductivity, large surface area, and enhanced electroactivity. This synergy is thus designed to enhance the composite's structural stability and electron transport, which are crucial for achieving good capacity, rate performance, and cycling stability in anodes. Conventionally, graphene is synthesized from non-renewable graphite precursors via energy-intensive processes. The development of sustainable and cost-effective routes for producing such advanced functional composite is therefore a critical research imperative [7,13].

In this context, lignocellulosic biomass waste has emerged as a promising renewable carbon precursor due to its abundance, low cost, and environmental sustainability. The conversion typically involves pyrolysis under an inert atmosphere, which carbonizes the biomass into a porous carbon structure that can be further graphitized at high temperatures. The chemical composition of the biomass—primarily cellulose, hemicellulose, and lignin—directly influences the yield

and structural properties of the resulting carbon. Cellulose, a linear polymer of glucose, provides a framework for carbonization. Hemicellulose decomposes at lower temperatures, influencing porosity. Lignin, with its high carbon content and aromatic structure, is particularly crucial as it yields a high char residue that facilitates the formation of a more ordered graphitic structure upon high-temperature treatment [14].

Puspa wood (*Schima wallichii*) is an excellent biomass source for this purpose. As a fast-growing species, it produces abundant sawdust as an industrial waste product. Critically, its lignocellulosic composition is highly favorable for carbonization: it contains approximately 51.2% cellulose, 21.8% hemicellulose, and 27% lignin. This balanced composition, with a significant proportion of rigid cellulose and high-carbon-yield lignin, makes it an ideal precursor for producing carbon materials with potential for graphitization. The trunk wood, where photosynthetic products are primarily stored, offers the highest biomass density and carbon content. The synthesis of reduced graphene oxide (rGO) from various biomass precursors, such as coconut shell, sugarcane bagasse, and lignin, has been actively explored as a sustainable alternative [22,25,35]. However, the direct, in-situ synthesis of a metal oxide/N-doped graphene nanocomposite from a single biomass source in a one-pot hydrothermal process remains a less-explored route. Despite its potential, the utilization of puspa wood sawdust for the direct synthesis of advanced carbon nanostructures like NDG, and specifically for MnO_2 /N-doped graphene (MnO_2 /NDG) composite, remains completely unexplored in the context of energy storage materials [14,15].

For the synthesis of such metal oxide/carbon composite, the hydrothermal method offers distinct advantages. It is a versatile, economical, and environmentally benign technique conducted in a sealed autoclave at elevated temperature and autogenous pressure [16]. The method enables the creation of well-defined nanostructures through reactions in an aqueous medium, requiring relatively low energy input, offering simple control over solution parameters, and minimizing equipment corrosion and chemical waste. These attributes make hydrothermal synthesis particularly suitable for the in-situ growth and

integration of different material phases, such as anchoring MnO₂ nanostructures onto a carbon matrix [17]. While composite of MnO₂ and carbonaceous materials have been studied, the in-situ one-pot hydrothermal synthesis of MnO₂ composite with NDG derived directly from this specific biomass waste remains unreported. Moreover, a systematic investigation into the effects of synthesis parameters (like GO concentration) on the structure and electrical properties of such biomass-derived composites remains limited.

Herein, we report a facile one-pot hydrothermal strategy, followed by sintering, for the synthesis of a MnO₂/NDG composite. In this approach, puspa wood sawdust serves as a sustainable carbon precursor for the in-situ formation of a nitrogen-doped carbon matrix. In contrast, urea serves as both a nitrogen dopant and a reducing agent. This design leverages the advantages of hydrothermal synthesis for intimate component integration, followed by sintering for structural consolidation. The study systematically investigates the effects of GO concentration and sintering conditions on the material's structural, morphological, and electrical properties [8,18,19]. We hypothesise that optimising these parameters will enhance the composite's electrical conductivity and structural integrity, which are essential prerequisites for developing high-performance anode materials.

Materials and methods

Materials

All chemicals were of analytical grade and used as received without further purification. Hydrochloric acid (HCl, 37%), sulfuric acid (H₂SO₄, 98%), potassium permanganate (KMnO₄, 99%), urea (CH₄N₂O, 99%), and sodium sulfate (Na₂SO₄, 99%) were purchased from Merck. Puspa wood was obtained from a local market. Deionized water was used throughout all experiments.

Instrumentations

The synthesis and characterization utilized the following instruments: digital balance (Ohaus), oven, 200-mesh sieve shaker, grinder, magnetic stirrer, hot plate, ice bath, beakers, measuring cylinders, pipettes, spatula, filter paper, ultrasonic probe sonicator (BIOBASE UCD-1000), 500 mL Teflon-lined autoclave, muffle furnace (Thermolyne), horizontal tube

furnace (Nabertherm RHTH 120/600), desiccator, X-ray diffractometer (SHIMADZU XRD-7000), Fourier Transform Infrared spectrometer (Perkin-Elmer Spectrum Two), UV-Vis spectrophotometer (UH5300), Transmission Electron Microscope with EDX analyzer (JEOL JEM-2100 Plus), hydraulic tablet press (TDP-5), copper foil, DC power supply (MDB-6050D), and digital multimeter (Krisbow).

Synthesis of graphite from puspa wood biomass

Puspa wood, sourced from a local Indonesian market, was processed to produce sawdust. The sawdust was subsequently oven-dried at 105 °C for two h and sieved to a maximum particle size of 1 mm [20]. An ultimate analysis was conducted on a sample of this sawdust to determine its initial carbon content [21]. To enrich the carbon content, the bulk of the sawdust was carbonised in a vacuum furnace at 600 °C for 3 h [22]. This was followed by graphitisation in a tube furnace. The temperature was raised from 600 °C to the target of 1,300 °C at a heating rate of 5 °C/min, held at 1,300 °C for 30 min, and then cooled naturally to room temperature within the furnace. This process promoted the formation of a crystalline graphite structure and further increased the carbon content [23]. The resulting graphite material was then ground and sieved to produce a fine powder with a particle size of 0.074 mm, a step taken to ensure suitable reactivity for further chemical processing and to attain the target properties of the final product [22]. For comparative benchmarking, graphite was also manually recovered from the anode of a spent commercial laptop lithium-ion battery. This recovered material underwent the same purification process (acid washing and drying) as the biomass-derived graphite and is referred to as "Graphite from LIB" in subsequent analyses.

For purification, the graphite powder was stirred in a 0.5 M hydrochloric acid (HCl) solution (employing a solid-to-liquid ratio of 1:10) at room temperature for 12 h to dissolve residual metal impurities. The purified solid was then thoroughly rinsed with deionised water until the filtrate reached neutral pH and finally dried at 105 °C for 3 h. The final purified graphite powder was characterized using ultimate analysis, X-ray diffraction (XRD), and Fourier-transform infrared (FTIR) spectroscopy.

Synthesis of GO via modified hummers method

GO was prepared from the purified puspa wood-derived graphite using a modified Hummers method. In a typical procedure, 1 g of graphite was combined with 0.5 g of sodium nitrate (NaNO_3) in 25 mL of concentrated sulfuric acid (H_2SO_4). The mixture was continuously stirred in an ice bath to maintain the reaction temperature below 20 °C. After 30 min, 3 g of KMnO_4 were added gradually under strict temperature regulation to prevent the temperature from exceeding 20 °C and to mitigate any excessive exothermic reaction. Stirring was sustained for 3 h, during which the solution turned dark green, indicating the oxidation of graphite. Subsequently, 50 mL of deionised water was slowly added to the mixture, and the temperature was raised to approximately 90 °C. Subsequently, an additional 100 mL of deionised water was added over 20 min while maintaining the temperature between 40 - 60 °C. The reaction was then quenched by the addition of 5 mL of hydrogen peroxide (H_2O_2).

The resultant mixture was allowed to stand overnight, after which it was filtered and washed repeatedly with deionised water until a neutral pH was attained, yielding graphite oxide (GrO). The obtained GrO was dried in an oven at 50 °C overnight [22,24,25]. For exfoliation into GO, the dried GrO was dispersed in deionised water at a concentration of 10 mg/60 mL and subjected to probe sonication for 1 h. The resulting dispersion was filtered, and the collected GO was dried overnight at 50 °C [26].

Synthesis of MnO_2/NDG

GO was dispersed in deionised water at three initial GO masses: 10, 15, and 30 mg, with each quantity suspended in 60 mL of water. Each dispersion was sonicated at 150 W for 30 min to ensure homogeneity. Subsequently, 0.316 g of KMnO_4 and 1 g of urea were introduced into each suspension, followed by stirring at 300 rpm for 20 min using a magnetic stirrer [26].

The resulting mixture was transferred to a 500 mL Teflon-lined autoclave and heated at 120 °C for 12 h. The solid product obtained from this process was collected, washed repeatedly with deionized water, and dried in an oven at 60 °C for 12 h to ensure complete moisture removal, yielding the final MnO_2/NDG composite [27]. From the 3 composite prepared, the sample exhibiting the highest electrical conductivity

was selected for further analysis. This chosen composite was characterized using Transmission Electron Microscopy (TEM), FTIR, XRD, and UV-Vis Spectroscopy.

Characterization materials

The moisture and ash content of the puspa wood sawdust were measured according to ASTM standards E871-80 and E1755. Ultimate analysis (CHNS) was performed using a Perkin-Elmer 2400 analyzer to determine the carbon, hydrogen, nitrogen, and sulfur content of the samples. The crystal structures and phase identification of the synthesised materials were analysed using XRD (SHIMADZU MAXima XRD-7000). Functional groups and chemical bonding were investigated using FTIR (Perkin-Elmer UATR Spectrum Two). The optical properties and band gap energy of the MnO_2/NDG composite were evaluated using a UV-Vis double beam spectrophotometer (UH5300). Morphology, particle size, and elemental distribution were examined using a transmission electron microscope equipped with an energy-dispersive X-ray spectroscopy (TEM-EDX, JEOL JEM-2100 Plus).

Conductivity test

The dried MnO_2/NDG composite powder were pressed into pellets with a diameter of approximately 1 cm and a thickness of about 0.1 cm using a hydraulic press. The pellets were then sintered in a furnace under an inert atmosphere. In the first optimization step, pellets from a fixed precursor formulation were sintered at different temperatures (400, 450, 500, and 550 °C) for 1 h to determine the optimal sintering temperature. Pellets with the 0.167 mg/mL GO formulation at 400 °C and 450 °C were damaged during processing and could not be measured. In the subsequent step, pellets with varying GO concentrations were sintered at the optimized temperature (550 °C) for 1 h. After sintering, the samples were slowly cooled to room temperature within the furnace to prevent thermal shock. The electrical conductivity of the sintered pellets was measured using a two-point probe method connected to a DC power supply (MDB-6050D) and a digital multimeter (Krisbow). Measurements were conducted by applying a voltage of 1 - 3 V and recording the corresponding output current. The two-point DC

method is a standard technique for measuring the resistivity of highly resistive materials, such as our composite pellets [28]. It was chosen because it directly measures the steady-state electronic conduction relevant to battery operation. While the total resistance measured includes contact contributions, the method provides a reliable, functionally relevant comparative metric for optimising the composite's conductive network, the primary goal of this study.

Results and discussion

Characterization of puspa wood biomass

The suitability of puspa wood sawdust as a carbon precursor was evaluated through proximate and ultimate analysis. The results, as shown in **Table 1**, indicate a carbon (C) content of 43.98%, hydrogen (H) of 7.408%, nitrogen (N) of 0.27%, sulfur (S) of 0.045%, and oxygen (O) of 48.297% (by difference). This carbon content is favorable and indicates a promising potential for high carbon yield, as will be contextualized by the comparative analysis below. The moisture and ash content were determined to be 10.596% and 1.256%, respectively. To evaluate its comparative potential, these properties are contrasted with other common biomass feedstocks in the same table. The carbon content of puspa wood is higher than that of sugarcane

bagasse (43.38%) and rice husk (35.8%), though slightly lower than coconut shell (47.17%) and oil palm shell (46.68%). This substantial carbon content is a primary indicator of its potential for high carbon yield during pyrolysis. The notably high hydrogen content (7.408%) suggests a significant proportion of volatile compounds, which can influence the porosity and reactivity of the resulting carbon material. Importantly, the nitrogen and sulfur contents are relatively low (0.27% and 0.045%, respectively), minimizing the risk of generating NO_x and SO_x pollutants during high-temperature treatment and favoring the production of cleaner carbon material. The moisture content of 10.596% is within an acceptable and workable range for biomass processing. While it necessitates a dedicated drying step (as implemented in this study at 105 °C) to ensure efficient pyrolysis, it does not significantly detract from the overall process or the quality of the final carbon product. A key advantageous finding is the low ash content of 1.256%, which is significantly lower than that of rice husk (16.3%) and oil palm shell (7.75%), and comparable to sugarcane bagasse (1%). A low ash content is highly desirable as it implies minimal inorganic residue after carbonization, leading to a carbon product with higher purity and potentially better electrical conductivity [29-33].

Table 1 Comparison properties of puspa wood with others biomass.

Biomass Sources	C (%)	H (%)	N (%)	S (%)	O (%)*	Moisture (%)	Ash (%)	References
Puspa wood	43.98	7.408	0.27	0.045	48.297	10.596	1.256	This study
Sugarcane bagasse	43.38	6.13	0.20	0.05	50.24	7.95	1.00	[28]
Coconut shell	47.17	6.50	0.21	0.04	46.08	12.00	3.40	[29]
Rice husk	35.80	5.80	0.25	0.06	58.09	9.50	16.30	[30]
Oil palm shell	48.68	6.16	0.22	0.05	44.89	15.21	7.75	[31]

*Calculated from the difference

XRD analysis of carbonized charcoal and derived graphite

Figure 1 presents the XRD diffractograms of the intermediate and final products: carbonized charcoal, graphite before washing, and graphite after washing. For direct crystalline reference, the standard diffraction peak positions of highly ordered standard graphite (JCPDS Card No. 00-012-0212) are indicated by vertical tick marks in **Figure 1**. The carbonised charcoal exhibits a

predominantly amorphous structure, typical of biomass-derived carbon and resulting from the complex composition of the lignocellulosic precursor [22]. A significant structural evolution is observed after graphitization at 1,300 °C. The diffractograms of both the washed and unwashed graphite samples show a sharp and dominant peak in the range of $2\theta = 23.50^\circ$ to 26.50° . In graphite crystallography, the (002) plane corresponds to the characteristic interlayer spacing

between stacked graphene layers. This peak indicates the development of a more ordered graphitic structure, corresponding to the (002) plane of graphite. The transition from a broad, amorphous scattering profile to a sharp (002) diffraction peak provides direct evidence

for the formation of periodic, long-range structural order along the c-axis, confirming the evolution of graphitic domains. The presence of this sharp peak, in contrast to the amorphous profile of the charcoal, confirms the successful conversion to graphite [25].

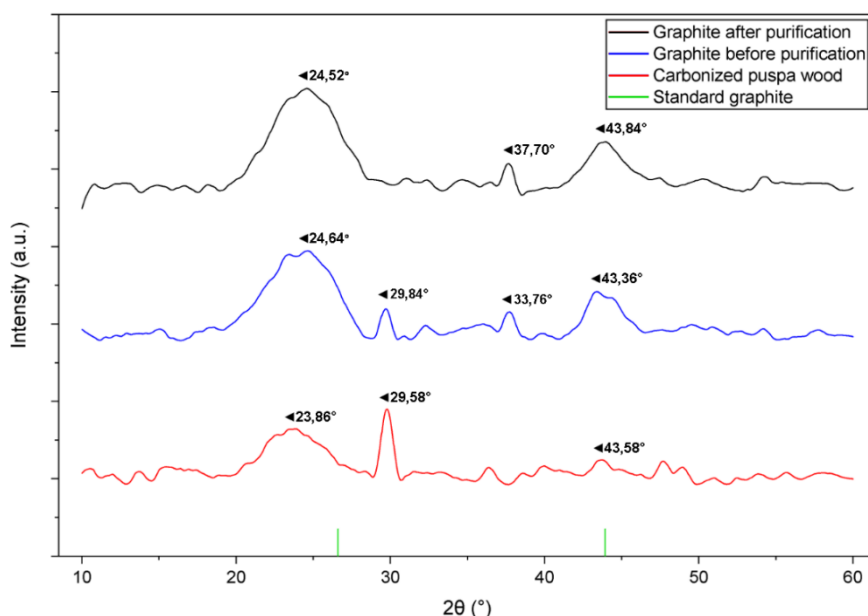


Figure 1 XRD patterns of carbonized charcoal (amorphous), graphite before washing (sharp (002) peak at $\sim 26^\circ$, impurity peak at 29.8°), and graphite after washing (purified). Tick marks indicate standard graphite peaks (JCPDS No. 00-012-0212).

In the context of carbon materials derived from biomass, the emergence of this distinct (002) peak is widely recognized as indicative of graphitization, and the resulting material is conventionally termed “graphite” despite the processing temperature being lower than that required for perfect crystallinity. The presence of this sharp peak, in stark contrast to the amorphous profile of the charcoal, confirms a successful conversion to a turbostratic graphite phase [22,25]. The broadening of the (002) and (100) peaks, compared to highly crystalline standard graphite, indicates a lower degree of graphitization. This is a common characteristic of graphite derived from biomass precursors, as the complex lignocellulosic structure and limited processing conditions typically yield a more turbostratic carbon with smaller crystallite sizes. Nevertheless, the distinct and sharp (002) peak confirms a significant transition from amorphous charcoal to a sufficiently ordered graphitic phase for its intended use as a precursor for graphene oxide synthesis.

The diffractogram of the unwashed graphite sample reveals an additional peak at $2\theta = 29.82^\circ$, attributed to calcium carbonate (CaCO_3) from inherent biomass minerals. This peak is absent in the HCl-washed sample, demonstrating the effectiveness of the acid purification step in removing inorganic impurities and yielding a phase-purer graphite [25]. A minor peak at $2\theta = 37.70^\circ$ is observed in both graphite samples, likely due to a minor reaction with the Al_2O_3 crucible at the high graphitization temperature [34]. Furthermore, a feature in the range of $2\theta = 43.00^\circ$ to 44.00° suggests structural rearrangement into a more ordered graphite lattice [22].

FTIR analysis of carbonized charcoal and derived graphite

FTIR spectroscopy was employed to track the chemical transformation from charcoal to graphite and to identify the functional groups present. The spectra of puspa wood-derived charcoal and graphite (before and

after acid washing) are presented in **Figure 2**. The charcoal spectrum displays a broad absorption band in the 3,400 - 3,600 cm^{-1} region, characteristic of O-H stretching vibrations from hydroxyl groups [35,36]. These groups originate from the cellulose, hemicellulose, and lignin components of the biomass [37,38]. Additional key peaks confirm the presence of

various organic functional groups: a peak at 1,705 cm^{-1} (C=O stretching of acetyl/aldehyde groups), 1,571 cm^{-1} (aromatic C=C stretching), 1,406 cm^{-1} (C-H bending), 1,174 cm^{-1} (C-O-C stretching), and 780 - 858 cm^{-1} (aromatic C-H bending). This profile is typical of partially carbonized biomass containing residual polymeric structures and oxygenated groups [39-42].

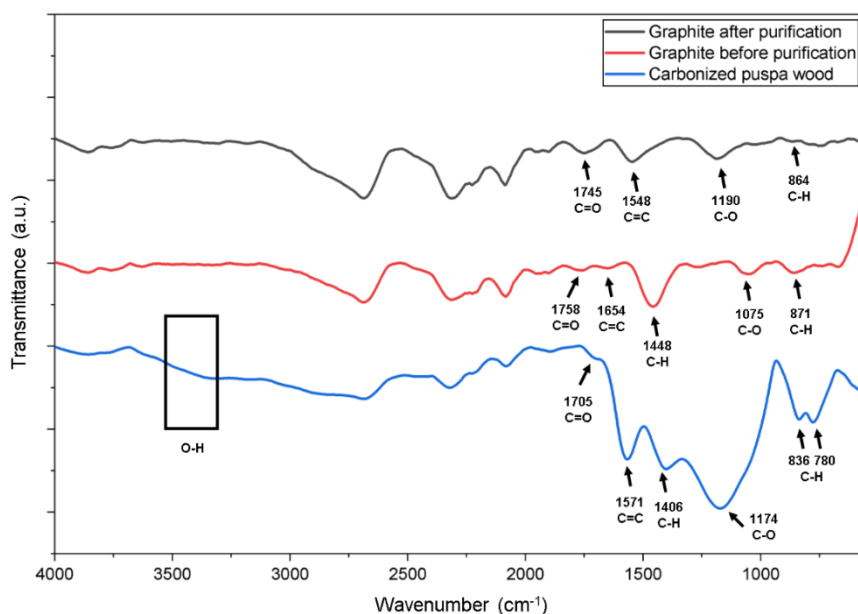


Figure 2 FTIR spectra of charcoal, unwashed graphite (reduced oxygen peaks), and washed graphite (cleaner carbon signature).

A stark contrast is observed in the graphite spectra. The complete disappearance of the broad O-H band (3,400 - 3,600 cm^{-1}) confirms the effectiveness of the high-temperature graphitization process (1,300 °C) in thoroughly decomposing the lignocellulosic structure and removing hydroxyl groups [43]. Furthermore, oxygen-related peaks are significantly diminished. The C=O peak is weakened and shifted (to ~1758 cm^{-1} for unwashed and ~1745 cm^{-1} for washed graphite), while the intensity of other oxygen-containing bands drops markedly. The peaks associated with aromatic C=C bonds (now appearing at ~1,654 cm^{-1} and ~1,548 cm^{-1}) become more defined and symmetrical, indicating the formation of a more ordered and homogeneous graphitic network [43,44]. The reduction in intensity of peaks in the 1,400 - 1,460 cm^{-1} region (C-H bending) suggests the decomposition of residual lignin fragments [40,46].

The comparison between unwashed and washed graphite reveals the impact of acid purification. It should be emphasised that hydrochloric acid washing does not

chemically modify the graphitic carbon framework; rather, it primarily removes residual metal oxides and inorganic mineral impurities originating from the biomass precursor and the graphitisation process. The washed graphite spectrum shows a further reduction in oxygenated functionalities and a clearer profile, as the removal of these inorganic impurities minimizes associated or adsorbed oxygen species, revealing a cleaner carbon signature. Only minor residual C-O stretching visible around 1,065 cm^{-1} [47-49]. The small peak near 864 - 871 cm^{-1} (aromatic C-H) persists in both graphite samples, though less intense than in charcoal, confirming the aromatic backbone and higher graphitization degree [40,42].

XRD analysis of GrO and GO

The successful oxidation of the purified puspa wood-derived graphite to GrO and GO were confirmed by XRD, as shown in **Figure 3**. The diffractogram of the GrO intermediate exhibits a prominent, sharp peak at 2θ

$\approx 10 - 11^\circ$, which is the characteristic (001) diffraction peak of GO. This peak indicates a significant increase in the interlayer spacing (d-spacing) relative to pristine graphite, due to the intercalation of oxygen-containing functional groups (e.g., hydroxyl, epoxy, carboxyl) between the carbon layers during oxidation [50]. The

XRD patterns of the GrO intermediate and the final exfoliated GO are virtually identical, confirming that the subsequent sonication step primarily induces physical exfoliation into thinner sheets without altering the fundamental oxidized crystal structure.

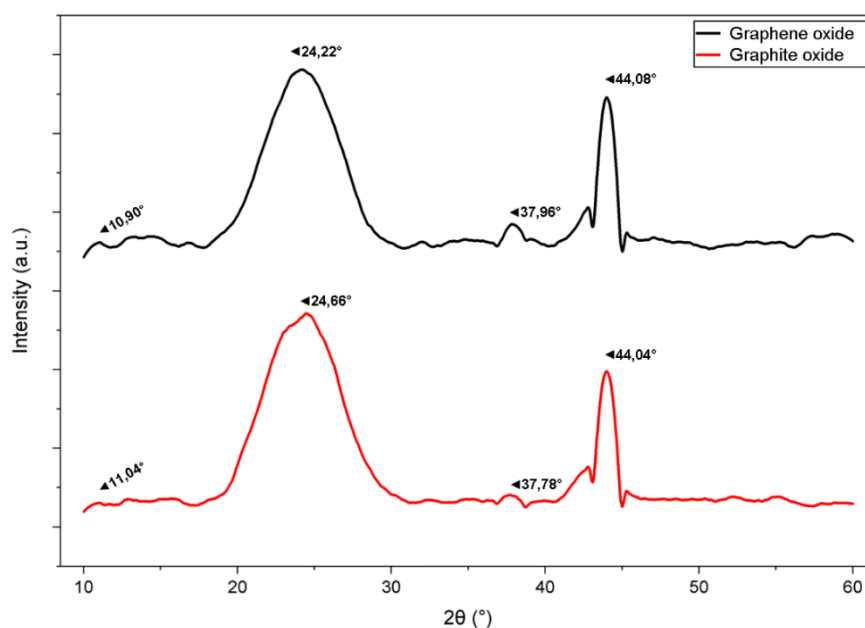


Figure 3 XRD patterns of graphite oxide (GrO) and graphene oxide (GO), both showing characteristic (001) peak at $\sim 10^\circ - 11^\circ$ confirming successful oxidation.

This distinct low-angle peak confirms the successful oxidation of graphite into GrO and GO, with expanded interlayer spacing due to oxygen functional groups. However, the diffractogram also reveals residual peaks at approximately $2\theta \approx 25^\circ$ and 43° , corresponding to the (002) and (100) planes of graphitic carbon, respectively. This indicates that the oxidation process was not complete, resulting in a material that is a mixture of fully oxidized GO sheets and partially oxidized, less-ordered graphitic domains [51-53]. The detection of a minor, broad feature in the 2θ range of $36 - 38^\circ$ may be attributed to trace amounts of manganese oxide (e.g., MnO_2) phases, likely formed from residual KMnO_4 used as the oxidant during the synthesis [54]. In summary, XRD analysis verifies the synthesis of GrO and GO from biomass-derived graphite. The material consists primarily of oxidized, layered sheets with an expanded interlayer distance, though it retains some residual graphitic character,

which is typical for GrO and GO produced via chemical oxidation methods.

FTIR analysis of GrO, GO and NDG

The chemical transformation from GrO to GO and, finally, to NDG was further investigated by FTIR spectroscopy, as shown in **Figure 4**. The spectra of GrO and GO are remarkably similar, as sonication primarily causes physical exfoliation rather than significant chemical alteration. Both GrO and GO exhibit a broad absorption band in the $3,400 - 3,600 \text{ cm}^{-1}$ region, confirming the presence of abundant hydroxyl ($-\text{OH}$) groups introduced during the oxidation process [25]. The strong peaks at approximately $1,704 \text{ cm}^{-1}$ (GrO) and $1,711 \text{ cm}^{-1}$ (GO) are attributed to the stretching vibrations of carbonyl ($\text{C}=\text{O}$) groups in carboxyl or ketone functionalities, a hallmark of the Hummers method of oxidation [22,55]. The peak near $1,565 \text{ cm}^{-1}$ corresponds to the skeletal vibration of unoxidized graphitic domains ($\text{C}=\text{C}$), indicating that the oxidation

process did not completely disrupt the aromatic carbon network [56,57]. The peak around $1,202\text{ cm}^{-1}$ is assigned to the stretching vibration of C–O–C bonds in epoxy and alkoxy groups, which are characteristic oxygen-containing functional groups formed on the

basal plane of graphene oxide during chemical oxidation. The similarity between the GrO and GO spectra confirms that sonication successfully exfoliated the material without introducing new functional groups [35,49].

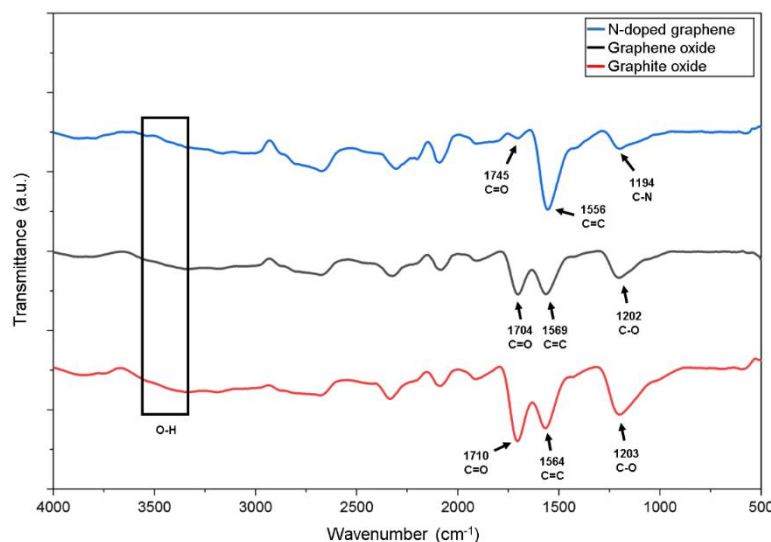


Figure 4 FTIR spectra of GrO, GO, and NDG. GrO and GO show O–H, C=O, and C–O–C peaks. NDG shows reduced oxygen peaks and emerging C–N features, confirming nitrogen doping.

In contrast, the NDG spectrum shows a distinct chemical shift. The intensity of the oxygenated functional groups (O–H, C=O, C–O–C) decreases significantly. Crucially, new features emerge, confirming successful nitrogen doping. The peak around $1,566\text{ cm}^{-1}$, while still present from the C=C backbone, can now also be associated with contributions from C=N or C–N stretching in heterocyclic structures [53,58,59]. More definitively, the appearance of a new, prominent peak at approximately $1,200\text{ cm}^{-1}$ is assigned to the stretching vibration of C–N bonds. This peak indicates the successful replacement of some C–O bonds with C–N bonds during the hydrothermal doping process with urea. The overall reduction of oxygen peaks and the emergence of nitrogen-related peaks demonstrate the effective reduction of GO and the simultaneous incorporation of nitrogen atoms into the graphene lattice, forming the targeted NDG material [59]. This confirmed incorporation of nitrogen (C–N bonds) enhances the electron-donating capability of the carbon matrix, contributing to the improved electrical conductivity measured for the MnO_2/NDG composite.

Table 2 The effect of sintering on electrical conductivity.

Optimization of electrical conductivity

The optimization of electrical conductivity followed a two-step design, first varying sintering temperature and then GO concentration. For context, a comparative sample of graphite recovered from a spent LiB (“Graphite from LIB”) was also tested. The conductivity results for the temperature variation in **Table 2** show a consistent increase with temperature, culminating in the highest value at $550\text{ }^\circ\text{C}$. Data for the 0.167 mg/mL GO composite at $400\text{ }^\circ\text{C}$ and $450\text{ }^\circ\text{C}$ are not available (N/A) due to pellet damage during preparation for those specific conditions. This trend is attributed to the enhanced reduction of GO into more conductive rGO and improved inter-particle connectivity at elevated temperatures, which collectively facilitate electron transport throughout the composite matrix. Therefore, $550\text{ }^\circ\text{C}$ was selected as the optimal sintering temperature.

GO concentration (mg/mL)	Electrical Conductivity (S/cm)			
	400 °C	450 °C	500 °C	550 °C
Graphite from LIB	8.4460 $\times 10^{-3}$	7.2380 $\times 10^{-3}$	8.1170 $\times 10^{-3}$	3.8870 $\times 10^{-7}$
0.167	0.2870 $\times 10^{-3}$	0.4391 $\times 10^{-3}$	N/A	N/A
0.250	0.0182 $\times 10^{-3}$	0.0468 $\times 10^{-3}$	0.0622 $\times 10^{-3}$	0.1832 $\times 10^{-3}$
0.500	0.0397 $\times 10^{-3}$	0.0683 $\times 10^{-3}$	0.2691 $\times 10^{-3}$	0.3906 $\times 10^{-3}$

*Note: Bold highlight the best result

Subsequently, with the sintering temperature fixed at the optimal 550 °C, the influence of GO concentration was investigated by synthesizing composite with varying GO loadings: 0.167, 0.25, and 0.5 mg/mL. The conductivity data in **Table 3** reveal a distinct percolation threshold, with the highest conductivity (3.38×10^{-5} S/cm) observed at the lowest concentration (0.167 mg/mL). This measured bulk conductivity, while inclusive of contact resistance, serves as a key indicator of the composite’s ability to form a percolating electron pathway—a property directly relevant to its function as an electrode material. This optimized conductivity represents a substantial enhancement of approximately two orders of magnitude compared to the poor intrinsic conductivity of pristine manganese dioxide materials (e.g., $\sim 10^{-7}$ S/cm) [60]. This significant improvement unequivocally demonstrates the critical role of the NDG matrix in forming a percolating conductive network that effectively bridges the α -MnO₂ nanorods, thereby addressing the fundamental limitation of poor charge transport in metal oxide-based anodes. To contextualize the electrical performance of the optimized MnO₂/NDG

composite (3.38×10^{-5} S/cm), a comparison with relevant reference materials is presented. Pristine MnO₂ exhibits intrinsically poor conductivity, typically in the range of $\sim 10^{-7}$ S/cm, which severely limits its application as an anode material [60]. The two-order-of-magnitude enhancement observed in our composite confirms the effectiveness of the NDG network in forming a percolating conductive pathway. For broader context within biomass-derived carbon materials, a conductivity of 2.06×10^{-5} S/cm has been reported for LiOH-modified activated carbon (Li/AC 2/1) derived from coconut shell [61]. Our result is comparable to this value, indicating that the incorporation of MnO₂ into the NDG matrix yields conductivity values comparable to those of pure carbonaceous anodes derived from similar biomass precursors. While direct comparisons with other MnO₂/graphene composites are limited—as most studies prioritize electrochemical metrics over absolute conductivity values—the achieved conductivity demonstrates a successful balance between the high capacity of MnO₂ and the charge transport required for electrode applications.

Table 3 Optimized electrical conductivity performance.

Material	Electrical Conductivity (S/cm)
Graphite from LIB (400 °C)	8.4460 $\times 10^{-3}$
GO Concentration 0.167 mg/mL (550 °C)	0.0379 $\times 10^{-3}$
GO Concentration 0.250 mg/mL (550 °C)	0.0278 $\times 10^{-3}$
GO Concentration 0.500 mg/mL (550 °C)	0.0294 $\times 10^{-3}$

At this optimal loading, the rGO forms a continuous, well-dispersed conductive network that effectively bridges the MnO₂ nanoparticles, creating efficient electron pathways while maintaining sufficient exposure of MnO₂ active sites for electrochemical reactions. This optimal morphology is achieved because the low GO concentration enables effective exfoliation and dispersion during synthesis, preventing sheet restacking and agglomeration. The well-dispersed rGO sheets can then uniformly coat and interconnect the MnO₂ nanoparticles, establishing a continuous conductive percolation network that facilitates electron transport between the otherwise poorly conductive metal oxide particles. The significant drop in conductivity at 0.25 mg/mL indicates a disruption in the percolation network, likely due to suboptimal dispersion where rGO sheets form isolated clusters rather than a connected pathway. Although conductivity partially recovers at 0.5 mg/mL, it does not exceed the optimum,

suggesting that while a high carbon content can eventually form some interconnected pathways, it may also lead to excessive MnO₂ coating and increased tortuosity [62].

XRD analysis of the optimized MnO₂/NDG

The crystal structure and phase composition of the optimized composite (550 °C, 0.167 mg/mL GO) were confirmed by XRD analysis, as shown in **Figure 5**. The diffractogram exhibits distinct and well-defined peaks that can be indexed to the hollandite-type α -MnO₂ phase (JCPDS No. 44-0141). The characteristic peaks at $2\theta \approx 12.83^\circ, 18.15^\circ, 28.55^\circ, 37.59^\circ, 42.09^\circ, 45.13^\circ, 49.43^\circ, 55.15^\circ, 59.87^\circ, 65.79^\circ, 69.07^\circ$ correspond to the crystal planes of a monoclinic α -MnO₂ structure. This tunnel-structured α -MnO₂ (2 $\times$ 2) is particularly advantageous for energy storage applications due to its high structural stability and the presence of open channels that facilitate rapid ion diffusion [54,63].

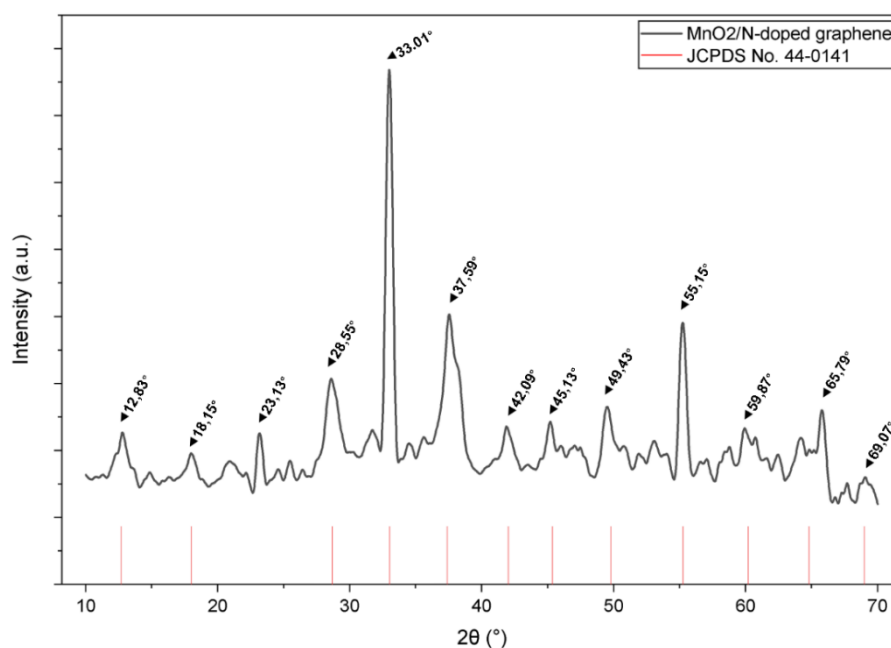


Figure 5 XRD pattern of MnO₂/NDG composite indexed to α -MnO₂ (hollandite, JCPDS No. 44-0141). Broad hump at $\sim 23^\circ$ corresponds to rGO.

In addition to the MnO₂ peaks, a broad and low-intensity hump centered around $2\theta \approx 23.13^\circ$ is observed. This feature is attributed to the (002) plane of rGO or graphitic carbon from the NDG matrix. The significant shift of this peak from the typical GO position ($\sim 10 - 11^\circ$) to a higher angle confirms the effective reduction of GO during the hydrothermal and sintering processes.

A sharp diffraction peak at $2\theta \approx 33.01^\circ$ is also observed, which does not correspond to α -MnO₂ (hollandite, JCPDS File No. 44-0141) and is attributed to a minor Mn₂O₃ phase, likely formed via partial reduction of MnO₂ during synthesis or post-treatment. No other significant crystalline impurity peaks are detected,

indicating that the composite is predominantly composed of α -MnO₂ [58,64].

FTIR analysis of the MnO₂/NDG before and after sintering

The chemical bonding and thermal stability of the optimised MnO₂/NDG composite were investigated using FTIR spectroscopy; spectra recorded before and after sintering are shown in **Figure 6**. Both spectra share similar absorption profiles, confirming the retention of the composite's fundamental chemical structure after thermal treatment. The prominent peak observed around 1,600 cm⁻¹ is attributed to the aromatic C=C stretching

vibration of the sp²-hybridised carbon network in the graphene backbone. This indicates that the essential conductive graphene structure is preserved despite nitrogen doping and composite formation with MnO₂. A peak at approximately 1,404 cm⁻¹, associated with C-H bending vibrations, is present in the unsintered sample. The most distinctive feature in the composite spectra is the broad, strong absorption band below 700 cm⁻¹, specifically in the 500 - 600 cm⁻¹ region. This band is characteristic of the stretching vibrations of Mn-O bonds, providing direct evidence for the successful formation and incorporation of manganese oxide within the composite [53].

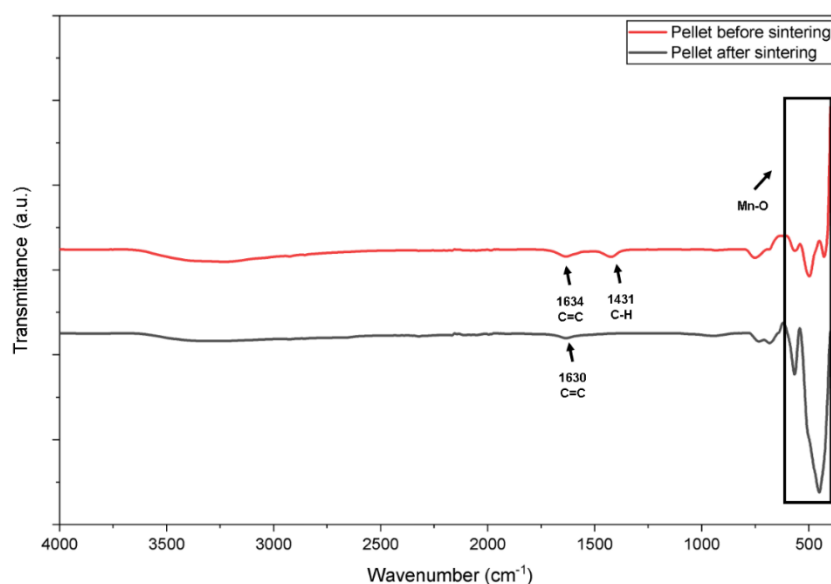


Figure 6 FTIR spectra of MnO₂/NDG before and after sintering. Both show Mn–O bonds (500 - 600 cm⁻¹) and C=C (1,600 cm⁻¹). After sintering, the C–H peak decreases and Mn–O band sharpens.

The sintering process induced significant changes in the FTIR profile, highlighting its role in enhancing the material's properties. The intensity of the C-H peak (1,404 cm⁻¹) decreases substantially after sintering, indicating the thermal decomposition and removal of residual hydrogen-containing groups, which are often unstable and can hinder electrical conductivity. Concurrently, the Mn-O absorption band becomes sharper and more intense. This change suggests an increase in the crystallinity of the MnO₂ phase and a strengthening of the Mn-O bonds, which is consistent with the improved structural order observed in XRD. The absence of any new significant peaks confirms that sintering does not introduce new functional groups but

rather refines the existing structure by removing unstable moieties and improving the interfacial bonding between the MnO₂ nanoparticles and the NDG matrix. This thermal stabilization is crucial for achieving a robust and highly conductive composite anode material [65,66].

Optical properties and band gap analysis

The optical properties and electronic structure evolution of the MnO₂/NDG composite, before and after sintering, were investigated using UV-Vis spectroscopy in **Figure 7**. The spectra provide critical insights into the effects of thermal treatment on the composite's chemical bonding and electronic conjugation. The

unsintered composite exhibits a single, broad absorption band centered around 767 nm. This band is characteristic of the d-d or charge-transfer (CT) transitions within the Mn-O framework of manganese dioxide, indicating the presence of MnO₂. The broadness of the peak suggests a semi-crystalline or amorphous nature of the MnO₂ phase at this stage. Notably, no distinct absorption peak is observed in the UV region (200–350 nm), which is typically associated with the $\pi \rightarrow \pi^*$ transitions of a conjugated carbon network. This absence implies that the GO precursor has not been fully reduced; its sp² carbon structure remains disrupted by residual oxygenated functional groups (C=O, C-O), hindering electron delocalization [67].

A dramatic change is observed in the spectrum of the sintered composite. Two well-defined absorption

features emerge: a sharp peak at approximately 287 nm and a prominent band around 772 nm. The peak at 287 nm is attributed to the $\pi \rightarrow \pi^*$ transition of the conjugated aromatic system in reduced, NDG. The significant redshift of this peak from the typical position for pristine GO (~230 nm) provides direct spectroscopic evidence of successful nitrogen doping. The incorporated nitrogen atoms donate electrons to the carbon lattice, increasing electron density and delocalisation within the π -system, thereby shifting the absorption to a longer wavelength. The appearance of this strong peak confirms that sintering effectively reduces GO, restores the sp²-hybridized carbon network, and integrates nitrogen into the graphene matrix [68].

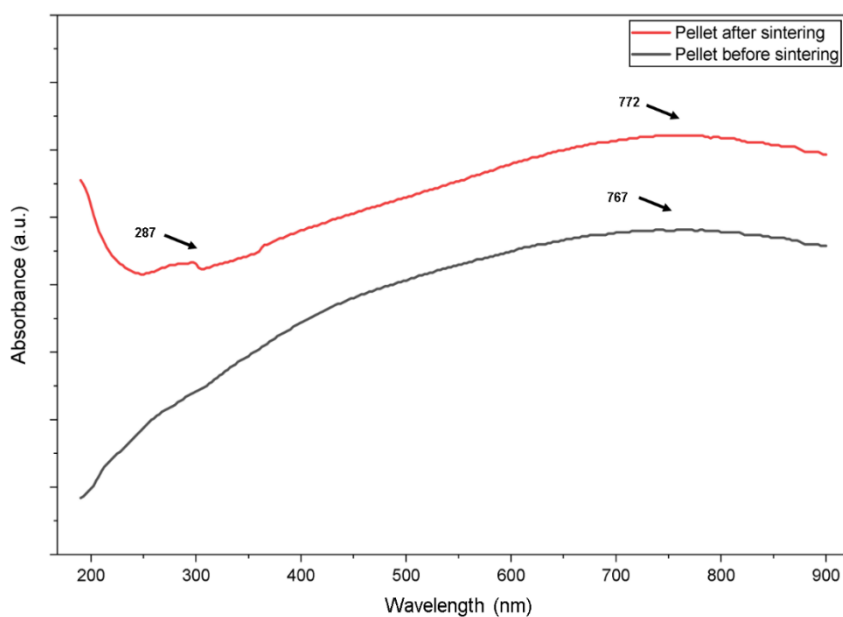


Figure 7 UV-Vis spectra of MnO₂/NDG before and after sintering. Sintered sample shows $\pi \rightarrow \pi^*$ peak at 287 nm (Restored Conjugation) and Mn–O band at 772 nm.

The persistence and intensification of the ~772 nm band after sintering indicates the retained and improved crystallinity of the MnO₂ phase, as supported by XRD and HRTEM results. The stronger absorption suggests enhanced interfacial interaction and charge transfer between the now more crystalline α -MnO₂ nanorods and the conductive NDG sheet. This extended absorption into the visible and near-infrared regions indicates improved optoelectronic properties, which are beneficial for charge transport in electrochemical applications [69].

The correlation between FTIR and UV-Vis results is consistent. The removal of C-H and oxygenated groups (as evidenced by FTIR) during sintering directly restores the π -conjugated system, as shown by the emergence of a strong $\pi \rightarrow \pi^*$ transition peak in UV-Vis. This synergistic analysis confirms that sintering is a crucial step for chemically reducing the composite, enhancing its structural order, and optimizing its electronic properties, which are essential for its function as an anode material.

Morphological analysis of MnO₂/NDG

The microstructure, crystallinity, and elemental distribution of the optimized MnO₂/NDG composite were analyzed using TEM, high-resolution TEM

(HRTEM), selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDS) mapping.

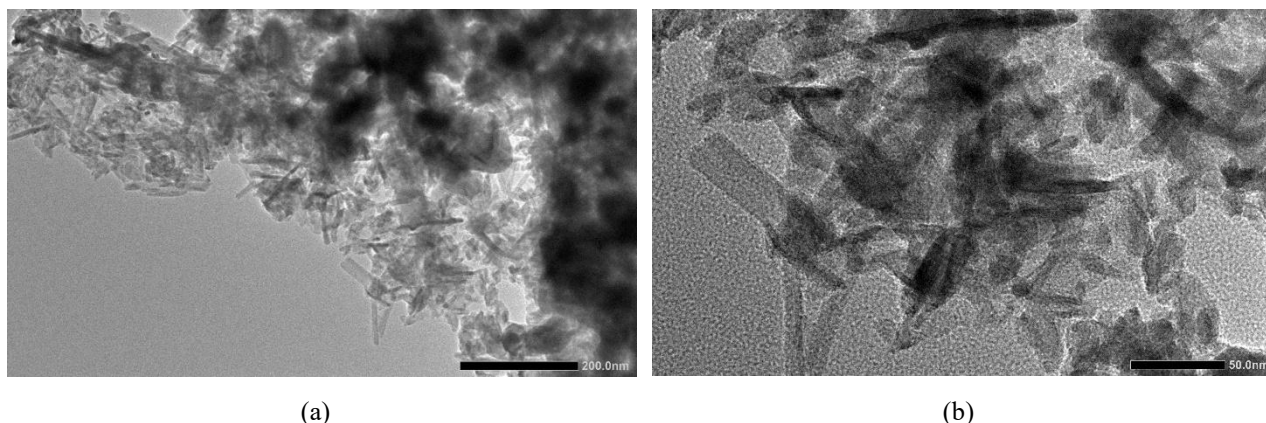


Figure 8 TEM images of MnO₂/NDG at (a) 200 nm showing uniform dispersion of nanorods on graphene sheets, and (b) 50 nm showing MnO₂ nanorods with width of approximately 50 nm.

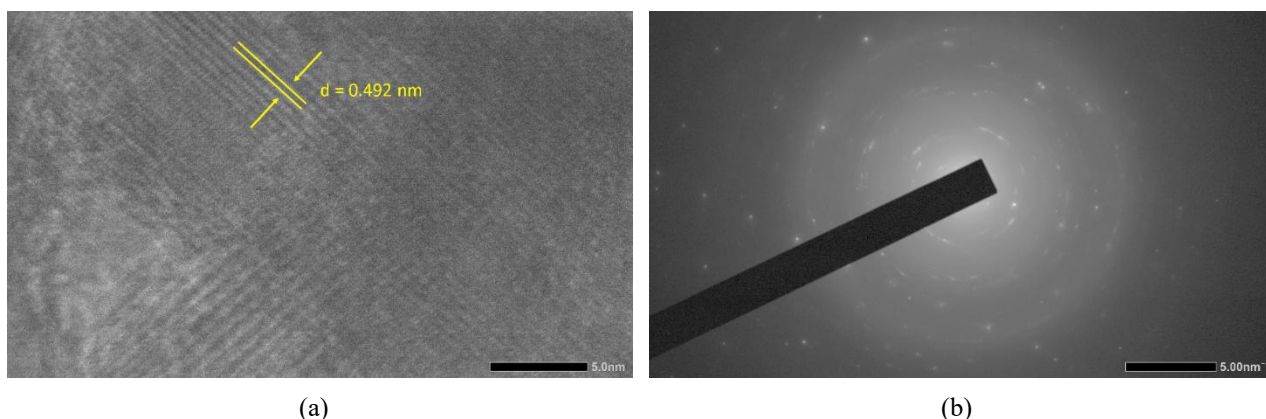


Figure 9 (a) HRTEM image showing lattice fringes (0.492 nm) corresponding to α -MnO₂ (200) plane. (b) SAED pattern with concentric rings indexed to α -MnO₂.

Morphology and structure

Low-magnification TEM (**Figure 8(a)**) images reveal a uniform distribution of dark, rod-shaped nanoparticles over large, transparent sheets, confirming the successful integration of MnO₂ nanostructures onto the graphene matrix. Higher magnification (**Figure 8(b)**) reveals nanorod-shaped particles with a width of approximately 50 nm. These particles are identified as crystalline α -MnO₂ based on the phase identification from XRD (**Figure 5**), which confirms the hollandite (α -MnO₂) structure—a phase known to crystallize in a nanorod morphology. The HRTEM (**Figure 9(a)**) image provides definitive structural evidence, displaying clear lattice fringes with an interplanar spacing of 0.492 nm.

This spacing corresponds to the (200) plane of hollandite-type α -MnO₂ (JCPDS No. 44-0141), which is consistent with the XRD results. The SAED pattern (**Figure 9(b)**) exhibits distinct concentric rings, characteristic of a polycrystalline material. The calculated d-spacings from the SAED rings (3.02, 1.92, 1.65, 1.38, 1.20, and 1.08 Å) match the major diffraction planes of α -MnO₂, further confirming the tunnel-type hollandite phase as the dominant crystalline component in the composite [53].

Elemental composition and distribution

EDS point analysis quantifies the elemental composition of the composite, revealing Mn (25.85

wt%), O (28.81 wt%), C (44.5 wt%), and N (0.83 wt%). The detection of nitrogen confirms the successful incorporation of N atoms into the carbon framework during the hydrothermal process with urea. It should be noted that the primary enhancement in electrical conductivity is governed by the GO concentration (percolation network) rather than the nitrogen doping content. As illustrated in the conductivity data (**Table 3**), the optimal conductivity is achieved at the lowest GO concentration (0.167 mg/mL). At this concentration, the rGO sheets form a continuous conductive network resembling a carpet-like structure on which MnO₂ nanorods are uniformly dispersed, creating efficient

electron pathways. At 0.25 mg/mL, the rGO sheets tend to encapsulate the MnO₂ particles, isolating them and disrupting the percolation network, resulting in a significant drop in conductivity. At 0.5 mg/mL, although the rGO sheets also encapsulate the MnO₂, the thicker rGO layers allow some particle-to-particle contact, partially recovering the conductivity but not exceeding the optimal value. The incorporated nitrogen atoms (0.83 wt%) play a supporting role, potentially contributing to improved charge carrier density within the NDG network, which synergizes with the percolating conductive pathway to yield the optimized conductivity measured in this study.

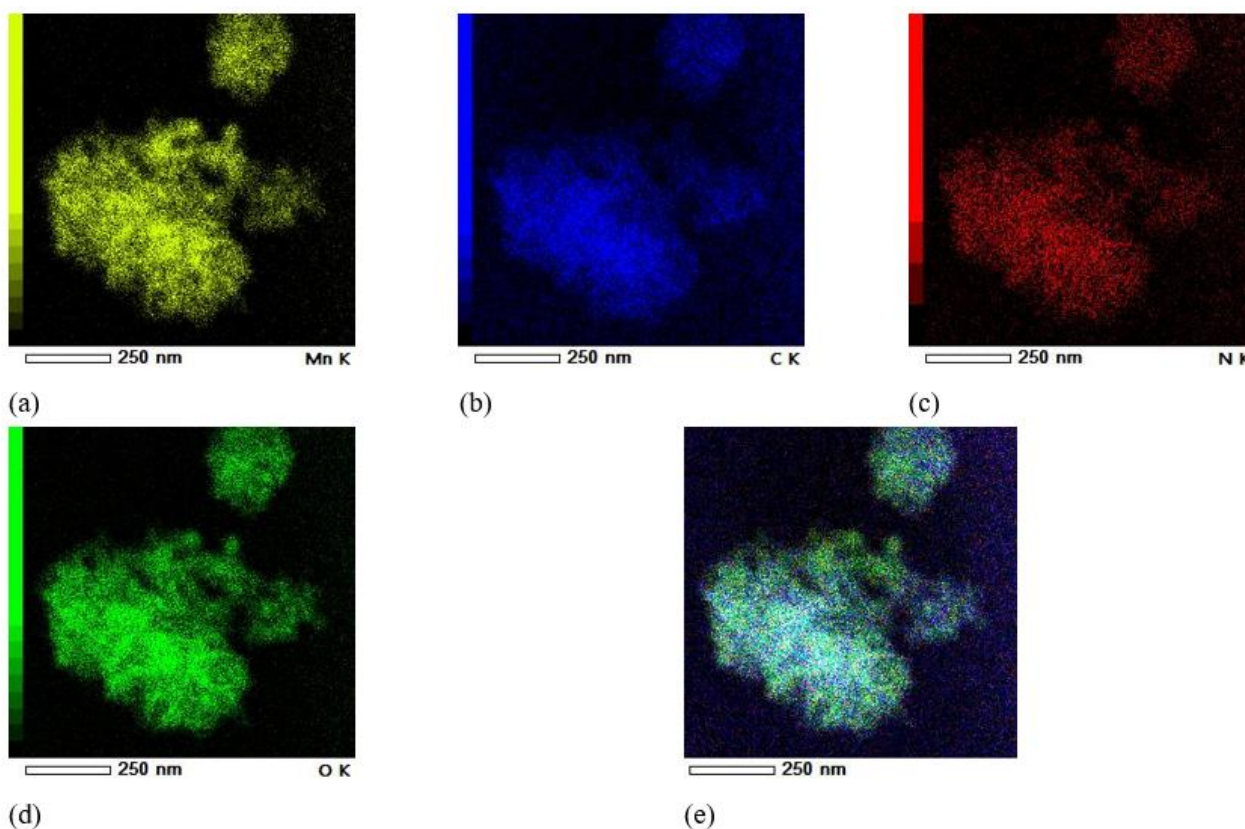


Figure 10 EDS elemental mapping of MnO₂/NDG: (a) Mn, (b) C, (c) N, (d) O, (e) overlay. Mn and O overlap in nanorod regions (MnO₂), C is widespread (graphene), N is uniform (successful doping).

Elemental mapping (**Figure 10**) provides a visual confirmation of the homogeneous distribution of all constituent elements. The signals for Mn and O overlap strongly in the regions corresponding to the nanorods, confirming their identity as MnO₂. The carbon signal is widespread, reflecting the continuous, sheet-like morphology of the underlying NDG matrix that forms a conductive scaffold throughout the composite, as seen in the TEM overview (**Figure 8(a)**), while the nitrogen

signal is uniformly distributed across the entire mapped area, indicating successful N-doping throughout the carbon matrix and potentially at the MnO₂/NDG interface. In conclusion, the comprehensive TEM analysis confirms the successful synthesis of a homogeneous composite where crystalline α -MnO₂ nanorods are firmly anchored and evenly dispersed on the surface of NDG sheets. This intimate contact and uniform elemental distribution are critical for

facilitating electron transport and ensuring structural stability, which are fundamental prerequisites for effective electrode performance.

Conclusions

This study demonstrates a green, sustainable route for synthesising a MnO₂/NDG composite from puspawood sawdust biomass. The sawdust was effectively converted into graphite, which was subsequently converted into graphene oxide. The optimal composite was obtained via a one-pot hydrothermal process with a GO concentration of 0.167 mg/mL and sintering at 550 °C, yielding the highest electrical conductivity among all tested conditions. Comprehensive characterization confirmed the successful formation of crystalline α -MnO₂ nanorods uniformly anchored on an NDG matrix, with strong interfacial interaction and restored π -conjugation indicating favorable charge transport pathways. These findings demonstrate the potential of puspawood as a biomass precursor and validate the feasibility of this route to fabricate structurally integrated MnO₂/NDG composites. The material's structural and electrical properties are highly relevant for the development of anode materials for LiBs. Therefore, comprehensive electrochemical evaluation, including galvanostatic charge-discharge and cycling tests, constitutes the essential next step to definitively assess its lithium storage performance.

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CRediT author statement

Muhammad Gibran Arrasyid: Methodology, Investigation, Software, Writing - Original Draft, Formal analysis, Visualization. **Widayat:** Conceptualization, Validation, Resources, Validation, Supervision, Writing - Review & Editing.

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