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Synthesis and Characterization of Reduced Graphene Oxide from Nipah Shell Charcoal (*Nypa fruticans* Wurmb) using Microwave Irradiation

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Abstract

Graphene, an allotrope of carbon, consists of a single layer of carbon atoms arranged in a honeycomb lattice and holds significant potential for diverse applications. This study focuses on the synthesis of reduced graphene oxide (rGO) from nipah shell charcoal (*Nypa fruticans* Wurmb) using a modified Hummer's method combined with microwave irradiation, employing L-ascorbic acid as the reducing agent. The synthesized rGO was characterized using Fourier Transform Infrared (FTIR) spectroscopy, X-ray Diffraction (XRD), and Scanning Electron Microscopy coupled with Energy Dispersive X-ray analysis (SEM-EDX). The FTIR spectra revealed an aromatic C=C ring stretching vibration at 1591.47 cm^{-1}. The XRD analysis showed characteristic rGO peaks at $2\theta \sim 27.58°$ and $48.45°$. SEM images indicated that the rGO exhibited sheet-like structures with slight wrinkling. Elemental analysis identified carbon and oxygen as the primary elements in both GO and rGO, alongside trace impurities, including N, Mg, Al, Si, Ca, Zn, and S. An increase in the C/O ratio from 1.90 in GO to 2.38 in rGO confirmed the successful synthesis of reduced graphene oxide.

1. Introduction

Graphene is a two-dimensional carbon allotrope consisting of a single atomic layer of carbon atoms arranged in a honeycomb (hexagonal) crystal lattice [1, 2]. Its potential applications are vast, including use in nanocomposites, adsorbents, sensors, photonic pollution control, electrodes, and solar cells, among others [2, 3]. Graphene can be chemically synthesized by oxidizing graphite into graphene oxide (GO) using strong oxidizing agents, followed by a reduction process to produce reduced graphene oxide (rGO) [4].

The Hummers method is the most widely used chemical exfoliation technique for producing GO from graphite. In this study, a modified Hummers method was employed, excluding $NaNO_3$ to prevent the generation of toxic gases during synthesis. GO can be reduced to rGO using hydrazine or its derivatives; however, these substances are highly toxic and unstable [5]. As a result, environmentally friendly reducing agents, such as L- ascorbic acid, have gained favor for rGO synthesis.

In addition to pure graphite, more economical natural and industrial carbon waste materials can serve as alternative sources for rGO production. These include plant waste (e.g., fruit peels, wood, leaves, and sugarcane bagasse), animal waste (e.g., bones and cow dung), paper waste, and industrial byproducts [6].

In this study, graphite was sourced from nipah shell charcoal (*Nypa fruticans* Wurmb). While nipah fruit is commonly processed into syrup and flour [7] or used for bioethanol production [8], the shells are often discarded as waste. Current applications of nipah shells include their use as activated carbon or adsorbents. A previous study [9] demonstrated that charcoal synthesized from nipah shell waste exhibited aromatic C=C absorption bands, confirming the formation of graphite. These findings suggest that nipah shell charcoal is a viable raw material for synthesizing rGO. To the best of our knowledge, the use of nipah shell charcoal as a source of graphite for rGO production has not been reported, highlighting the novelty of this research. Accordingly, this study focused on synthesizing rGO from nipah shell charcoal using chemical exfoliation. The process employed L-ascorbic acid (LAA) as an environmentally friendly reducing agent, with microwave irradiation to enhance the reduction process.

2. Experimental

2.1. Materials and Equipment

The materials used in this study included nipah shell charcoal from a previous study [9], phosphoric acid (H_3PO_4; 98%, Merck), sulfuric acid (H_2SO_4; 98%, Merck), potassium permanganate ($KMnO_4$; 98%, Merck), deionized water, hydrogen peroxide (H_2O_2; 30%, Merck), hydrochloric acid (HCl; 37%, Merck), ethylene glycol (99.5%, Merck), L-ascorbic acid (LAA, Merck), and ethanol (70%, Merck).

The equipment employed comprised glassware, a sonicator (E-Chrome UC-10200B), a Buchner funnel (Iwaki), an oven (Memmert UN110), a centrifuge (Ortoalresa Biocen 22R), an analytical balance (Shimadzu AP225W), a microwave (Toshiba), and a desiccator (Duran 247836955).

2.2. Synthesis of Graphene Oxide

GO was synthesized from nipah shell charcoal using a modified Hummers method [4, 6, 10, 11]. First, 3 g of nipah shell charcoal powder was mixed with 60 mL of a H_3PO_4 and H_2SO_4 solution in a 1:9 ratio and stirred. Subsequently, 9 g of $KMnO_4$ was gradually added to the mixture under continuous stirring, ensuring the temperature was maintained at 10°C. Following the addition of $KMnO_4$, 150 mL of deionized water was added, and the mixture was stirred at 35°C for 2 hours. The suspension was then left to oxidize at room temperature for 24 hours.

To terminate the oxidation process, 9 mL of 30% H_2O_2 was added to 300 mL of deionized water and introduced into the suspension. This mixture was allowed to react for 30 minutes. The resulting suspension was filtered using filter paper and washed with a solution of 5% HCl and deionized water in a 1:10 ratio to remove impurities. Purification and neutralization were performed using deionized water until the pH of the filtrate reached 7. Afterward, the suspension was centrifuged in two steps: first at 2000 rpm for 30 minutes and then at 8000 rpm for 60 minutes. Finally, the GO sample was dried at 60°C for 6 hours, yielding graphene oxide in powder form.

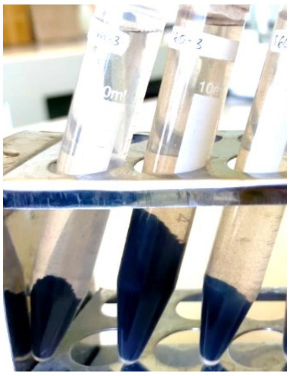


Figure 1. rGO suspension in deionized water

2.3. Synthesis of rGO

Two grams of GO powder were dispersed in 250 mL of ethylene glycol and sonicated for 2 hours. During sonication, 20 mL of 1 M LAA was gradually added as a reducing agent. Following the reduction process, the mixture was subjected to microwave irradiation at 800 W for 30 minutes. The resulting solution was filtered using filter paper and sequentially washed three times with deionized water and three times with ethanol. The obtained precipitate was then dried at 80°C for 4 hours, yielding rGO in solid form.

2.4. Characterization of GO and rGO

The synthesized GO and rGO samples were characterized using Fourier Transform Infrared Spectroscopy (FTIR, Bruker Alpha-P), X-ray Diffraction (XRD, Bruker D8 Advance), and Scanning Electron Microscopy coupled with Energy Dispersive X-ray analysis (SEM-EDX, JEOL JSM-6520LA).

3. Results and Discussion

3.1. Synthesis of rGO from Nipah Shell Charcoal

The primary material for rGO synthesis in this study was carbonized nipah shell charcoal. The synthesis process involved three main stages: oxidation, exfoliation, and reduction. Oxidation was achieved by adding $KMnO_4$ as an oxidizing agent in an acidic environment. During this stage, the color of the nipah shell charcoal transitioned from dark green to deep dark brown, indicating the progression of the oxidation process. The temperature was carefully maintained at 10°C to prevent the formation of manganese heptoxide (Mn_2O_7), a highly reactive and explosive compound that can form at temperatures above 55°C. The oxidation reactions are represented by Equations (1) and (2).

$$KMnO_4 + 3H_2SO_4 \rightarrow K^+ + MnO_3^+ + H_3O^+ + 3HSO_4^- \quad (1)$$

$$MnO_3^+ + MnO_4^- \rightarrow Mn_2O_7 \text{ [12]} \quad (2)$$

The exfoliation process was performed using sonication for 2 hours. Reduction was conducted by adding 1 M LAA as a reducing agent, followed by microwave irradiation. The microwaves generated heat within the sample, accelerating the reduction process. The successful reduction of GO to rGO was confirmed by the black coloration of the final product. The yield of rGO was 67.75% from an initial 2 g of GO. An image of the rGO suspension in deionized water is shown in Figure 1.

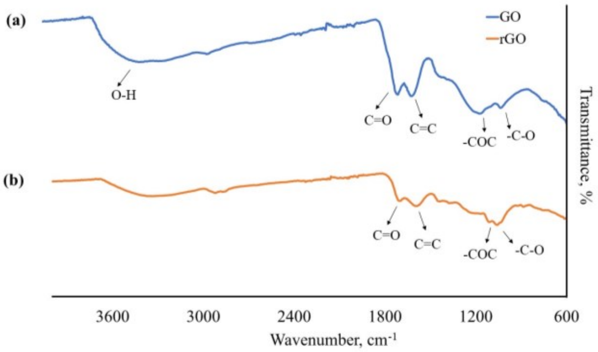


Figure 2. FTIR spectra of (a) GO and (b) rGO

Table 1. Absorption of functional groups in GO and rGO

ν GO (cm^{-1})	ν rGO (cm^{-1})	Functional group
3390.50	undetected	O-H hydroxy
1696.63	1703.84	C=O carbonyl
1606.66	1591.47	C=C aromatic
1167.03	1110.33	C-O-C stretching
1030.42	1059.67	C-O stretching

3.2. Characterization by FTIR Spectroscopy

Figure 2 displays the absorption peaks corresponding to the functional groups identified in both GO (a) and rGO (b) materials. In the GO spectrum, absorption was observed at a wavenumber of 1030.42 cm^{-1}, indicating the presence of C-O stretching bonds. The absorption peak at 1606.66 cm^{-1} corresponds to C-OH bending, while the peak at 1696.63 cm^{-1} represents C=O stretching, and the absorption at 3390.50 cm^{-1} is attributed to O-H stretching. After the reduction of GO to rGO (b), the -OH group in GO is reduced [13], resulting in the disappearance of the hydroxyl group absorption peak. Additionally, an aromatic C=C ring stretching was observed at 1591.47 cm^{-1}, which is characteristic of the reduced material [14].

3.3. Characterization by XRD Spectroscopy

Material characterization using XRD was performed to determine the crystallinity phases of GO and rGO. The XRD analysis results describe the material's characteristics based on the 2θ angle spectrum data obtained. The diffractograms for both GO and rGO are presented in Figure 3.

Based on the diffractogram patterns presented in Figure 3, a shift in the 2θ values between GO and rGO indicates successful reduction of GO to rGO. The diffraction peaks for GO are observed at 2θ = 10.8° and 23.55°, which is consistent with previous studies where the 2θ peaks for GO were found at 10.61° and 20.57° [15], and 10.783° and 24.6° [11]. The shift in these peaks may be attributed to residual impurities in GO, which could result from suboptimal oxidation.

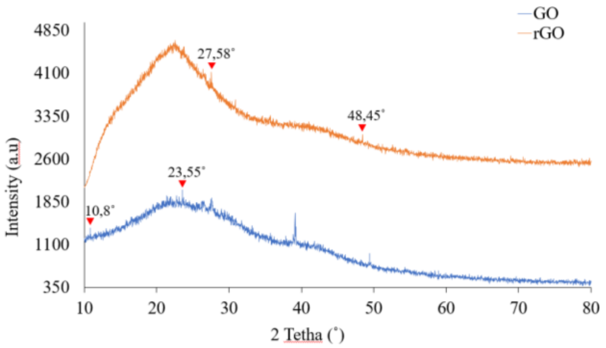


Figure 3. Diffractogram of GO and rGO

The reduction of GO to rGO is confirmed by the shift in the XRD peaks of rGO, observed at 2θ = 27.58° and 48.45°, suggesting that the reduction using LAA has been successfully carried out. These rGO peak positions align with previous reports, where peaks were found at 2θ = 24° and 43° [4], and 2θ = 26° and 44.5° [16]. Additionally, the characteristics of rGO fall within the typical 2θ range of 25°–28° [17]. The disappearance of the peak at 2θ = 10.783° further suggests that the GO layers have undergone exfoliation. The XRD patterns of both GO and rGO from nipah shell exhibit an amorphous phase, as indicated by the broadening of the diffractogram peaks.

3.4. Characterization by SEM-EDX Spectroscopy

To examine the morphology and elemental composition of GO and rGO materials, characterization was performed using SEM-EDX. The surface morphology of GO and rGO is presented in Figure 3. The SEM image of GO (Figure 4a) reveals a layered structure that is randomly and densely packed. After reduction to rGO, the surface morphology changes, with rGO appearing as sheets with slight wrinkles (Figure 4b).

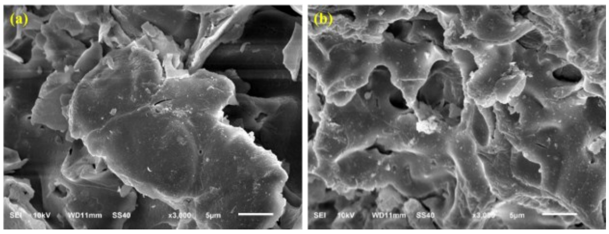
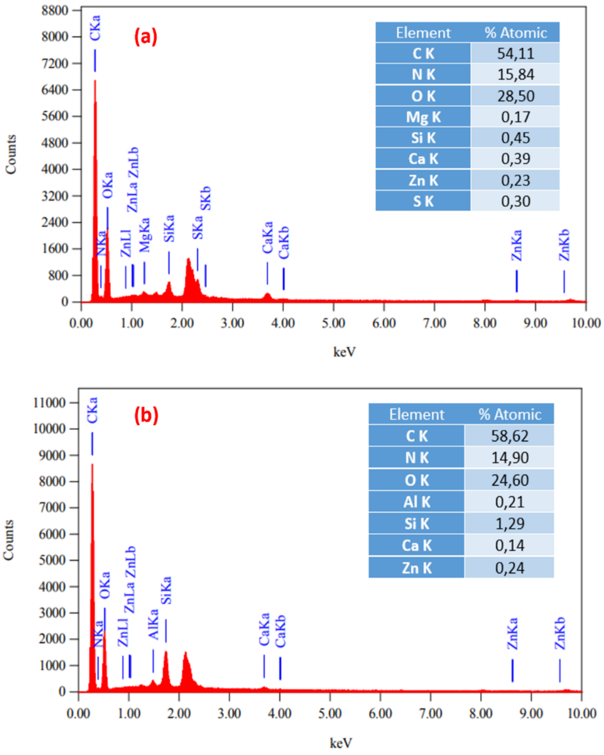


Figure 4. SEM images of (a) GO and (b) rGO



Element	% Atomic
C K	54,11
N K	15,84
O K	28,50
Mg K	0,17
Si K	0,45
Ca K	0,39
Zn K	0,23
S K	0,30

Element	% Atomic
C K	58,62
N K	14,90
O K	24,60
Al K	0,21
Si K	1,29
Ca K	0,14
Zn K	0,24

Figure 5. EDX spectra of (a) GO and (b) rGO

The elemental composition of GO and rGO, as determined by EDX analysis, is presented in Figure 5. Carbon (C) and Oxygen (O) are the primary elements in both GO and rGO, with the materials also containing trace amounts of impurities, including Nitrogen (N), Magnesium (Mg), Aluminum (Al), Silicon (Si), Calcium (Ca), Zinc (Zn), and Sulfur (S). The atomic percentage of nitrogen is notably significant in both GO and rGO, likely due to the carbon source, nipa palm shells, which are rich in inorganic elements.

The reduction of GO to rGO resulted in a decrease in the atomic percentage of oxygen, from 28.50% (for GO) to 24.60% (for rGO), and an increase in the C/O ratio from 1.90 (for GO) to 2.38 (for rGO). These values are lower than those reported by Bansal *et al.* [18], who found a C/O ratio of 2.51 for GO and 7.62 for rGO. The observed variation in the C/O ratio can be attributed to differences in the reduction processes used [19].

4. Conclusion

Reduced graphene oxide (rGO) derived from nipah shell charcoal has been successfully synthesized by reducing graphene oxide (GO) with L-ascorbic acid (LAA) under microwave irradiation. FTIR analysis revealed a characteristic peak for aromatic C=C bonds at 1591.47 cm^{-1}, confirming the formation of rGO. XRD analysis produced diffraction peaks at $2\theta = 27.58°$ and 48.45°, which are indicative of rGO material. SEM analysis showed a sheet-like structure with slight wrinkles on the surface of rGO. EDX analysis indicated that while the rGO contains several impurities, the C/O ratio remains relatively low.

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