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Research Article

Graphene oxide synthesis from coconut fiber powder using triple superphosphate catalyst and its potency for secondary battery electrode

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Abstract. Coconut fiber, considered an organic waste, emerges as a promising alternative carbon source for graphene oxide production—a material characterized by its conductive nature due to oxidation and the introduction of functional groups. The synthesis process involves carbonization with varied holding times (10, 20, and 30 minutes) and the utilization of Triple Superphosphate (TSP) and Ferrocene catalysts at concentrations of 10 wt.% and 20 wt.%. Subsequently, the sonication method is employed to enhance the electrical conductivity of graphene oxide post-carbonization. Notably, the electrical conductivity tests, conducted using a sourcemeter, revealed the optimum performance at 20 minutes of carbonization duration and a 20 wt.% TSP catalyst concentration, yielding an impressive electrical conductivity of 11,489.86 S/m. These findings underscore the significance of tailored parameters in optimizing graphene oxide synthesis for applications such as high-conductivity battery anodes.

Keywords: Carbonization, Coconut Fiber, Electrical Conductivity, Graphene Oxide, Sonication

1. Introduction

Lithium-ion batteries play a crucial role in meeting the escalating demand of today's society, as evidenced by the remarkable surge in global revenue generated by these batteries. In 2010, Electric Vehicle (EV) sales contributed a modest $200 million to the global income, but this figure skyrocketed to an impressive $66.2 billion in 2020 (Bank, 2009). This surge can be primarily attributed to the burgeoning market demand for Electric Vehicles, underscoring the indispensable role of lithium-ion batteries in various sectors, such as electronics, telecommunications, and the rapidly evolving electric automotive industry (Masias et al., 2021).

Lithium-ion batteries distinguish themselves as environmentally friendly, rechargeable secondary batteries, devoid of hazardous materials found in earlier battery technologies like Ni-Cd and Ni-MH (Assefi et al., 2020). Their superior energy storage stability, high energy density (offering up to 1000 charging cycles), relatively lightweight construction, and easy maintenance contribute to their widespread adoption (Costa et al., 2021).

The fundamental components of lithium-ion batteries include positive and negative electrodes (cathode and anode), electrolyte, and separator. The quality of electrodes, particularly the anode and cathode, is crucial for producing high-performance lithium-ion batteries. Materials with high conductivity, such as metals, are essential for fabricating quality electrodes (Yi et al., 2020). Graphite, a conductive material, serves as an anode in solid lithium battery cells, while graphene, with its unique properties like high surface area to volume ratio, exceptional electronic transport, and chemical stability, presents a promising alternative (Rezaei et al., 2020).

Graphene oxide, a precursor to graphene, boasts higher lithium storage capacity than graphite, outstanding chemical stability, and easy water dispersion (Tian et al., 2021). Unlike graphene, graphene oxide production is cost-effective as it does not necessitate reduction treatment (Zhang et al., 2013). Several methods, including the Hummers method, chemical vapor deposition (CVD), and sonication, can be employed to exfoliate graphite into graphene (Adetayo &

Runsew, 2019). The sonication method, utilizing ultrasonic waves in water, stands out for its simplicity, affordability, and scalability, despite generating some noise and lower purity graphene. Previous research encountered environmental and cost challenges in producing graphene oxide, prompting this study to adopt a cheap and eco-friendly approach. The synthesis technique integrates impregnation, foil layering, carbonization, and sonication, offering an efficient and straightforward process to derive graphene oxide from agricultural waste.

The primary raw material in this study is coconut fiber, chosen for its organic compounds such as lignin, cellulose, and hemicellulose. Given Indonesia's tropical climate and its status as a leading coconut producer, utilizing coconut fiber waste aligns with the abundance of this agricultural byproduct. According to Statistik Perkebunan Indonesia (2017), Riau province in Indonesia led coconut production with a staggering 392,701 tons, highlighting the significant potential for repurposing coconut fiber waste in graphene oxide synthesis.

This research endeavors to achieve three primary objectives. Firstly, it aims to discern the impact of varying carbonization holding times on the conductivity of synthesized graphene oxide. Secondly, the study seeks to elucidate the influence of different quantities of Triple Super Phosphate (TSP) on the conductivity of graphene oxide, providing crucial insights into the optimal dosage for enhanced conductivity. Lastly, the research explores the combined effects of TSP and Ferrocene on graphene oxide conductivity, aiming to uncover potential synergies between these additives. These objectives collectively form a comprehensive investigation into key parameters influencing the electrical properties of graphene oxide, with implications for refining synthesis processes and optimizing the material for diverse applications.

2. Method

2.1. Graphene Oxide Synthesis via Ferrocene-Catalyzed Wet Impregnation Process

The wet impregnation process aims to create a ferrocene solution for soaking coconut fiber powder. Initially, a 10 wt.% or 20 wt.% ferrocene solution is prepared by dissolving it in 200 ml of 96% pure technical ethanol. The dissolution occurs at 60 °C with a rotation speed of 200 rpm, and the beaker is covered with parafilm during homogenization to prevent volume shrinkage. Next, the weighed coconut fiber powder is soaked in the ferrocene solution for 24 hours. The heating and stirring process at 60 °C and 200 rpm ensures complete submersion, expedites the reaction, and enhances the diffusion of the ferrocene solution into the coconut fiber pores. Parafilm covers the beaker to prevent solution evaporation. After soaking, the sample is filtered using a tea filter to separate it from the filtrate. The filtered sample is placed in a beaker, covered with perforated aluminum foil, and dried in an 80 °C oven for 24 hours to eliminate residual ferrocene solution. Post-drying, the sample agglomerates, necessitating crushing to regain a powdered form. Following crushing, aluminum foil is used to coat the crucible in multiple layers (Figure 1). The crucible is coated with one layer of aluminum foil, followed by a second layer containing the crushed 2-gram sample, leaving 20% empty space for even heating. The third layer tightly covers the crucible's top with aluminum foil, and the final layer envelops the entire crucible surface. Subsequently, the sample undergoes carbonization at 900 °C in a tube furnace with a heat rate (HR) of 5 °C/minute. The carbonization holding time varies between 10, 20, and 30 minutes. An alumina tube, closed at both ends with rubber, is employed for this process. In the final stage, the graphene oxide sample is crushed using a mortar until passing through a 300-mesh sieve, aiming to achieve carbon particles of the desired size.

Figure 1. Foil sheet coating schematic

2.2. Graphene Oxide Synthesis Process using TSP Catalyst

The foil sheet coating in this synthesis process employs aluminum foil, similar to the previous sample. The coating is done in layers within the crucible. Initially, the first layer involves coating the crucible with a single layer of aluminum foil. Moving to the second layer, it is coated with TSP (thiourea dioxide) powder, with variations of 10 wt.% and 20 wt.% relative to the weight of coconut fiber powder. Subsequently, in the third layer, coconut fiber powder is placed atop the evenly spread TSP powder. The fourth layer involves tightly covering the crucible's top with aluminum foil, and in the final layer, the entire crucible surface is tightly covered using aluminum foil. An illustrative diagram of the foil sheet coating can be referenced in the provided image. The carbonization process's operational conditions mirror those of the previous sample. The process includes holding times ranging from 10 to 30 minutes at a temperature of 900 °C, with a heat rate (HR) of 5 °C/minute. The furnace tube and alumina tube, both in an airtight condition, remain consistent. To minimize air ingress into the alumina tube, both tube ends are sealed using rubber with a diameter tailored to the alumina tube's inner diameter. Following carbonization, the sample undergoes a grinding and sieving process to achieve small graphene oxide particles in line with the 300-mesh sieve size used. The objective is to obtain graphene oxide particles of the desired size through this sieving process.

2.3. Electrical Conductivity Measurement

After the carbonization and sonication treatment of the samples, the subsequent phase involves assessing their electrical conductivity through a source meter, facilitated by the KickStart software. To ensure the accuracy of the electrical conductivity values for graphene oxide, a crucial preliminary step involves drying the sample in an oven at 80oC. This precautionary measure prevents any decline in the conductivity values. For testing, a 0.45-gram sample is carefully placed into an empty holder, which is then positioned on four legs for compression using a torque wrench set to 10 kgf.cm. The two cables attached to the sample holder are connected to crocodile claws – the top cable to a black crocodile claw and the bottom cable to a red crocodile claw. Once both cables are securely connected, the test is initiated by clicking "execute test." Throughout the testing process utilizing the source meter, resistance values are measured in ohms (Ω). These values, derived from the test results, provide insights into the electrical conductivity characteristics of the graphene oxide sample. This systematic approach ensures a comprehensive analysis of the sample's electrical properties.

3. Result and Discussion

3.1. Mass Percentage of Graphene Oxide Produced

The mass percentage of graphene oxide serves as a key metric, representing the reduction in mass resulting from the carbonization process conducted at a temperature of 900 °C with a HR of 5 °C/minute. The research data outlines the mass percentage of graphene oxide with varying concentrations of TSP at 10 wt.% and 20 wt.% relative to the weight of coconut fiber powder. Carbonization holding times of 10 minutes, 20 minutes, and 30 minutes were employed to investigate the impact on mass percentage. The observed trend reveals a gradual increase in the mass loss rate with elevating carbonization temperature. This indicates that higher carbonization temperatures necessitate more time to reach the target temperature, consequently extending the overall carbonization process duration. The time taken to attain the designated temperature aligns with the duration of the carbonization holding time (Mohammed et al., 2018). In essence, the longer time required to reach and maintain the desired temperature contributes to an extended carbonization process. The research findings, specifically examining the influence of carbonization holding time on the mass percentage of graphene oxide, are visually presented in Figure 2. This graphical representation provides a clear insight into how varying carbonization parameters impact the resulting mass percentage, aiding in a comprehensive understanding of the carbonization process and its outcomes.

The decrease in the percentage of graphene oxide produced with increasing carbonization time can be caused by several factors. Increasing the carbonization time can result in material degradation due to exposure to high temperatures over a longer period of time. This can lead to loss of structural components that may contribute to the formation of graphene oxide (McDonald-Wharry et al., 2013). During a longer carbonization time, there is a possibility that more volatile components in the sample can evaporate. This can reduce the total mass of the sample and, consequently, lower the percentage of graphene oxide produced. Increasing the carbonization time may lead to purification of the carbon structure, and this may involve the elimination of more oxygen and non-carbon elements from the sample. This purification can reduce the number of oxygen groups and other functionalities that make it different from pure graphene. The carbonization process at high temperatures involves a large number of complex chemical reactions. Over time, these reactions can change and produce various byproducts. If these reactions are not regulated properly, they can reduce the amount of graphene oxide produced. If the sample is contained in solution during the carbonization process, a longer time may cause more evaporation of the solution. This can result in a decrease in the total mass of the sample and ultimately decrease the percentage of graphene oxide.

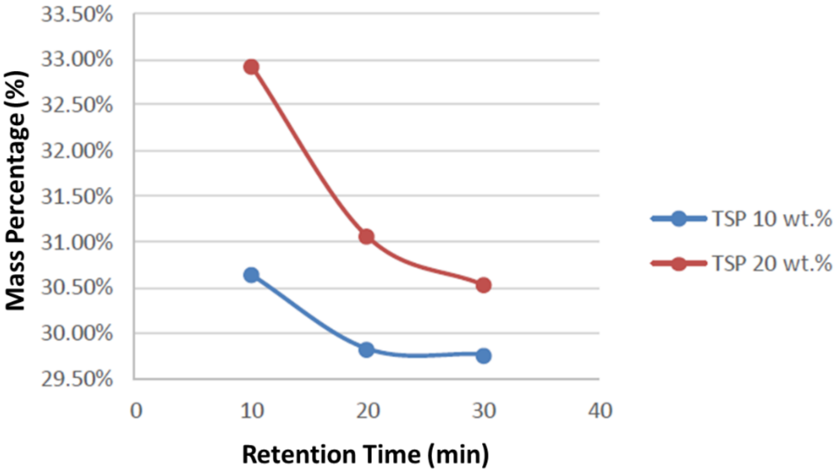

Figure 2. Mass percentage of graphene oxide at different carbonization retention times

3.2. Electrical Conductivity of Graphene Oxide

The electrical conductivity of a material is determined through testing using a sourcemeter, specifically the Keithley instrument. The primary objective of this testing is to measure the resistance of the material. The outcome of these measurements provides valuable data on the electrical properties of the material. Table 1 illustrates the results obtained from the measurements conducted with the sourcemeter. The findings indicate that, at a holding time of 20 minutes with a TSP concentration of 20 wt.%, the material exhibits the highest electrical conductivity value, reaching 11489.86 S/m. This result is noteworthy when compared to holding times of 10 minutes and 30 minutes, as well as a TSP quantity of 10 wt.%. The discernible variation in electrical conductivity values across different holding times and TSP concentrations underscores the influence of the holding time parameter on the resulting conductivity values.

With a catalyst concentration of 10%, an increase in retention time from 10 to 20 minutes leads to a rise in conductivity from 35.92 s/m to 43.58 s/m. Nevertheless, when the retention duration is extended to 30 minutes, the conductivity diminishes to 35.99 s/m. The first rise in conductivity may be attributed to the substance's contact with the column or separation medium, resulting in changes in conductivity. The following reduction might be ascribed to changes in the chemical composition or elution behavior of the examined components. When the catalyst concentration is increased to 20%, there is a notable enhancement in conductivity after 20 minutes, as shown by the values of 61.12 s/m at 10% concentration and 11489.86 s/m at 20% concentration. At the 30-minute mark, there is a significant reduction in conductivity, which measures at 35.12 s/m. The significant rise in conductivity seen as the concentration increases from 10% to 20% suggests a greater abundance of ions or conductive substances in the eluent at the higher concentration, maybe resulting from a change in the eluent's composition (Korkmaz & Kariper, 2020). The following decline in conductivity after 30 minutes may be attributed to the conclusion of the elution process or changes in the composition of the eluent.

Table 1. GO conductivity at various retention times and catalyst concentrations

Retention Time (min)	**Conductivity (s/m)**	
	10 wt. % TSP	**20 wt. % TSP**
10	35.92	61.12
20	43.58	11489.86
30	35.99	35.12

3.3. Graphene Oxide Comparison between TSP and Ferrocene Catalyst

The obtained results highlight a notable influence of holding time and catalyst type on electrical conductivity values in the synthesis process (Table 2). Specifically, at a 20-minute holding time and with a TSP concentration of 20 wt.%, the highest electrical conductivity value was recorded at 11489.86 S/m. This surpassed the conductivity values observed at both 10 and 30 minutes, as well as at a 10 wt.% TSP concentration. This underscores the significance of holding time as a crucial factor affecting conductivity outcomes. Furthermore, the research findings indicate a superior electrical conductivity performance with TSP catalyst compared to Ferrocene. Specifically, the electrical conductivity achieved with TSP was measured at 11489.86 S/m, whereas the Ferrocene catalyst yielded a lower conductivity of 28.07 S/m.

In the case of TSP and ferrocene catalysts, the differences in conductivity may arise from various factors, including the chemical structure, functional groups, and overall quality of the synthesized graphene oxide. TSP and ferrocene catalysts may lead to the introduction of different functional groups onto the graphene oxide sheets during the synthesis process. The type and density of functional groups can significantly affect the electrical conductivity of the material. The degree of oxidation of graphene oxide can influence its electrical properties. TSP and ferrocene may contribute differently to the oxidation process, resulting in variations in the number of oxygen-containing functional groups on the graphene oxide sheets. The presence of structural defects and disorder in the graphene oxide sheets can impact conductivity (De Silva et al., 2020). The catalyst used can influence the formation of defects and the overall quality of the graphene oxide, which in turn affects its electrical properties. Catalysts may affect the size and morphology of the graphene oxide sheets. Larger sheets with fewer boundaries may exhibit better electrical conductivity. The catalyst choice could influence the growth and arrangement of these sheets. The choice of catalyst may result in different doping effects on the graphene oxide sheets. Doping can introduce additional charge carriers, affecting the electrical conductivity of the material. Residual chemicals or impurities introduced during the synthesis process can impact the electrical properties. The type and amount of impurities may vary depending on the catalyst used.

When evaluating the economic aspect, TSP emerges as a cost-effective choice compared to ferrocene. The graphene oxide synthesis process using ferrocene demands more electrical energy, involving intricate steps such as wet impregnation, soaking, and drying processes. Additionally, the carbonization process with ferrocene results in a dirtier condition of alumina tube walls due to its lower melting point of 172.5 °C (Yerroju et al., 2022), in contrast to the cleaner process with TSP, which boasts a significantly higher melting point of 1583 °C. In essence, the comprehensive analysis underscores the superior electrical conductivity performance, cost-effectiveness, and cleaner processing associated with TSP catalyst, making it a preferable choice over ferrocene in the examined synthesis processes.

Table 2. Comparison of mass percentage and electrical conductivity of GO with TSP and Ferrocene catalysts

Catalyst (@ 20 wt. %)	Mass Percentage (%)	Conductivity (s/m)
TSP	31.06	11489.86
Ferrocene	30.50	28.07

4. Conclusion

This study conducted a series of experiments to investigate the synthesis of highly conductive graphene oxide. Here are few findings derived from this investigation. The graphene oxide exhibited the maximum electrical conductivity of 11489.86 S/m when subjected to a carbonization holding duration of 20 minutes. The electrical conductivity of GO is stronger when it is combined with a TSP catalyst containing 20 wt.% of GO, compared to a TSP catalyst containing 10 wt.% of GO. The electrical conductivity of graphene oxide GO when utilizing the transition metal-based TSP catalyst surpasses that of ferrocene. Given the existing limitations in this study, the following recommendations are proposed for further studies on this subject. To enhance the electrical conductivity of GO, it is advisable to optimize the sonication procedure. It is advisable to include the variable representing the amount of Triple Superphosphate employed in order to determine the optimal electrical conductivity value of the GO. For optimal results throughout the carbonization process, it is advisable to maintain airtight conditions in order to reduce the oxidation of the sample.

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