BIOSYNTHESIS OF GRAPHENE OXIDE NANOPARTICLES FROM COCONUT FRONDS

ABSTRACT

To address the ecofriendly approach for the nano graphene oxide (nGO) synthesis, "Wealth from waste" idea utilized in this study. The synthesis process involves the controlled reduction and manipulation of nGO sheets to achieve nano-scale dimensions, resulting in nGO with improved structural integrity and enhanced surface area. Characterization of the synthesized nGO is conducted using advanced analytical tools, including Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), UV-Visible spectroscopy (UV-VIS) and Particle Size Analyser (PSA). The PSA analysis revealed, a predominantly monodisperse distribution with a peak size of approximately 314 nanometers with indicative of good dispersion uniformity. The UV-Visible spectroscopy displayed a significant absorption peak at 234 nanometers, elucidating the material's optical characteristics. TEM images unveiled the structural features such as wrinkles, folds and nanoscale dimensions. The XRD diffractogram suggested the presence of both GO and rGO phases with unique intensity peaks. These analyses provide valuable insights into the morphology, size and crystallinity present in the nGO, aiding in its structural elucidation. These findings affirm the successful conversion of coconut fronds waste into GO nanoparticles and open avenues for sustainable nanomaterial production. The biosynthesis of nano graphene oxide particles offers exciting opportunities for the development of next-generation materials with enhanced performance characteristics.

Keywords: Graphene oxide, Coconut, Nanoparticles, TEM.

1. Introduction

Nanotechnology, a domain of science and technology has the essence and ability to build intricate patterns with fundamentally novel molecular organization by manipulating tiny molecules atom by atom. Montmorillonite with normal size and dimension will occupy the surface area of 30-40 m^2g^{-1} (Macht et al., 2011) when its reduced to nano by ball milling will have 750 m^2g^{-1} (Sharmila Rahale, 2010). "Wealth from waste" this idea has been utilized to address the environmental issue by challenging the conventional view of waste as finished goods that have to be used as a primary source for many things. Bio-based products are

currently considered options for large-scale production. Over 5 billion tons of crop residue (CR) is produced globally each year, due to increasing food demand and intensive agriculture(Shinde et al., 2022).

Coconut palm is also known as KALPAVRIKSHA (Tree of Heaven) because of its versatile nature and the multi-use of its products. In the world, India accounts for a third in the cultivation area (17.73%) and higher in production (30.93%) and productivity. A healthy coconut palm produces 12-15 fronds per year. At a time 30-35 fronds can hold in the crown of the palm. Wherein after their third-year, fronds start shedding approximately 566.90 crore fronds per year in India (Indiastat, 2022). These coconut fronds are employed in a variety of fields, including the production of art paper from chemical pulp (Faisal et al., 2020) promising material for biochar (Aziz et al., 2018), fish aggregation system attractants (Ibrahim et al., 2014), roofs for traditional homes and so on. Addition to these the totally dried fronds been used for this study though it's our duty is to ensure each tree is used to the fullness of its life. For enhancing this, the wastes from coconut palm wherein utilized for the synthesis of nano Graphene Oxide (nGO).

Graphene oxide (GO), so called "Miracle Material", is the oxidized form of graphene, which is a single-atomic-layered material of carbon atoms in a honeycomb pattern (Alam et al., 2017) , (Guerrero-Contreras & Caballero-Briones, 2015). It has oxygen-containing groups on the surface, such as epoxide, carbonyl, carboxyl, and hydroxyl which makes it has dispersible in water(Al-Maliki et al., 2022) and other solvents in which graphene can be synthesized. Graphene serves as the fundamental building block for all other dimensions of graphitic materials. The mechanical exfoliation process for large scale graphene production was not suitable. Consequently, scientific interest is growing in the reactively oxidizing chemical method of GO material which resemble graphene structurally.

Different approaches were available for the synthesis of graphene oxide nanoparticles. Among this Modified Hummer's approach was widely employed to create GO since it involves oxidising graphite by combining a graphite, potassium permanganate, sodium nitrate and sulfuric acid solution(Shahriary & Athawale, 2014). In our methodology, resembling Modified Hummer's with several changes were made to reduce the size and dimension of the particles will be seen. This straightforward, affordable, and renewable method for making nano graphene oxide may open up new possibilities for the manufacturing of graphene-based nanomaterials with several applications.

2. Materials and Methods

2.1. Chemicals and Raw materials

Chemicals used in this investigation were procured from Spar and utilized exactly as received. Waste Coconut fronds were gathered from a nearby farmer field. All experimental solutions, including the stock solution and dilutions, were made using double-distilled water. pH adjustments were made using 0.1M HCl and 0.1M NaOH as and when necessary.

2.2. Biogenic Nano GO Synthesis

2.2.1. Carbonization

The collected coconut fronds were washed, chopped, and solar-dried for 2-3 days by maintaining maximum temperature. And then once again dried in a Hot air oven at 100°C for 2 hours. Using silica crucible/basin CF samples were carbonized in a muffle furnace at 350°C for 2 hours. The sample was allowed to cool at room temperature (24-25°C) then with a pestle and mortar the samples were grind and sieved using 200 mesh size (≤74.5 µm).

2.2.2. Alkali Activation

Freshly prepared 50 ml of 2M NaOH was added to 5g of sieved carbonized sample(Grace & Malar, 2020) and kept stirring for 2 hours and then undisturbed for 15 hours. After 15 hours, the activated carbonized sample was oven dried at 100°C for 3 hours.

2.2.3. Synthesis of Graphite Oxide

The Modern Modified Hummers method (Arthi *et al.* 2015) was used to oxidize the prepared carbonized sample. The activated carbon powder (1g) and $NaNO_3$ (0.5 g) were added to a 250ml Erlenmeyer flask and then kept in an ice bath at 5-10°C. Then 25ml of conc. H_2SO_4 was poured and kept for stirring at 250rpm in a Magnetic stirrer for an hour. This was followed by slow addition of $KMnO_4$ (3g) by maintaining the temperature below 10°C with constant stirring for 2 hours where the solution turned dark green colour. After that it was removed from the ice bath and kept stirring for an hour at 35°C. At that time the colour changed from dark green to milk chocolate colour. Then deionized water (50ml) was slowly added using a dropper with continuous stirring for an hour where the solution turned dark brown colour with the appearance of bubbles indicating oxidation. Furthermore, addition of deionized water (100ml) to terminate the oxidation and stirred for 30mins followed by the

addition of 30% H_2O_2 (1.5ml) to remove excess $KMnO_4$ where the solution turns dark yellowish brown after 30mins of sterilization.

2.2.4. Synthesis of Nano Graphene Oxide

The solution obtained was then sonicated in an ultra-probe sonicator for an hour with a 10s pulse ON/OFF and 40% amplitude, which helps graphite oxide to exfoliate into graphene oxide and to reduce size. It was followed by centrifugation (5000rpm for 15mins) with distilled water for several washes until pH gets neutralized which effectively eliminated the remaining acids and contaminants from the solution. The supernatant solution was decanted and the precipitate was oven dried. The resultant product was nano Graphene Oxide (nGO) and it was characterized using instruments.

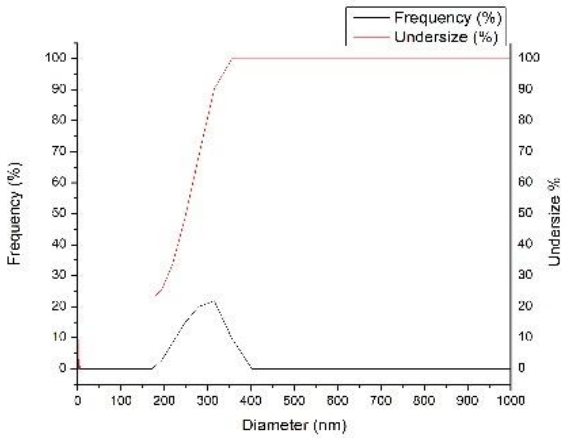
2.3. Characterization

The Graphene Oxide in regular and nano-size were characterized using particle size analyser, zeta sizer, powder X-Ray Diffraction, UV-Vis Spectroscopy and Transmission Electron Microscope.

3. Results and Discussion

Graphene Oxide Nanoparticles were successfully synthesized by Modern Modified Hummer's method from coconut frond wastes. The GO sample was acquired in two different forms: one as colloidal solution and other as powder. Particle Size Analyzer, TEM and UV-VIS spectroscopy were used to characterize the colloidal sample, whereas XRD and Raman Spectroscopy were used to characterize the powder sample.

3.1. Particle Size Analyzer



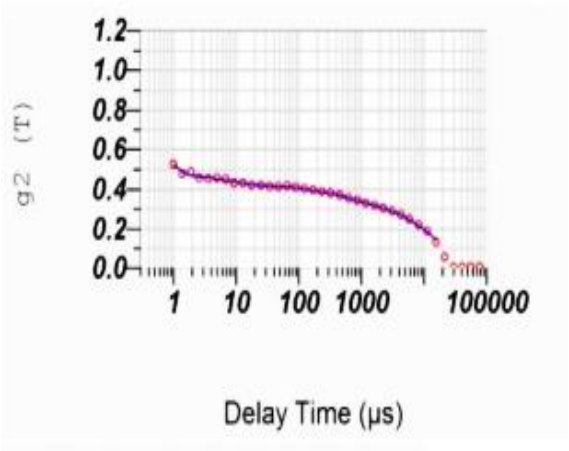


Figure 1 PSA of GO (Solution)

The size distribution histogram of GO sheets in solution, is depicted Figure 1. The histogram reveals, a predominantly monodisperse distribution with a peak at approximately 314 nanometers. The mean hydrodynamic diameter of the GO sheets was determined as approximately 314 nanometers. This value represents the average size of the GO sheets in the suspension. The PDI, a measure of the distribution width, was found as 1.728. A low PDI value indicates a relatively narrow size distribution, suggesting good uniformity in the dispersion. The zeta potential of the GO sheets in the suspension was -41.1 mV(Guo et al., 2022). This parameter provides information about the electrostatic stability of the dispersion. Hydrodynamic radius lies between 170 nm to 401 nm with a Gaussian peak at 314 nm.

3.2. UV-VIS Spectroscopy

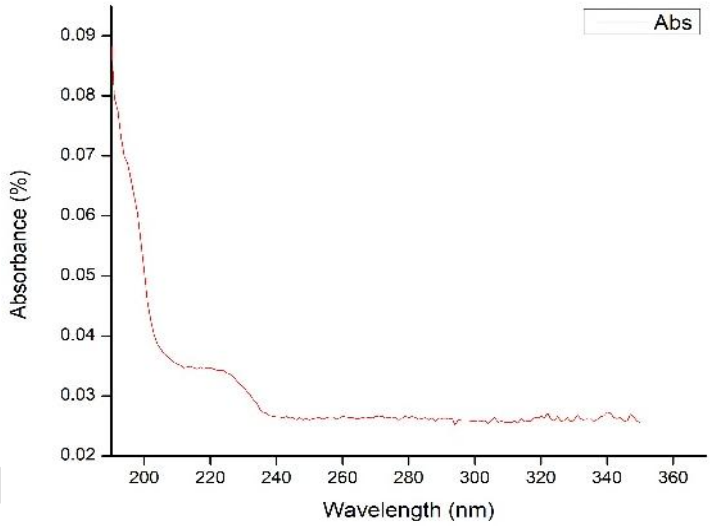


Figure 2. UV-VIS spectrum of GO (Solution)

The optical characteristics of GO was determined using UV-Visible Spectroscopy (Hasani et al 2018). The spectrum of absorbance is shown in Figure 2. The spectra illustrate the amount of light or energy absorbed in a colloidal solution by the GO particles synthesized from coconut frond waste, and it lies in 190-350 nm wavelength range. The absorption spectrum reveals a prominent absorption peak at 234 nanometers. This peak corresponds to the π-π* electronic transitions in the GO sheets(Sellathurai et al., 2023) .

3.3. Transmission Electron Microscopy

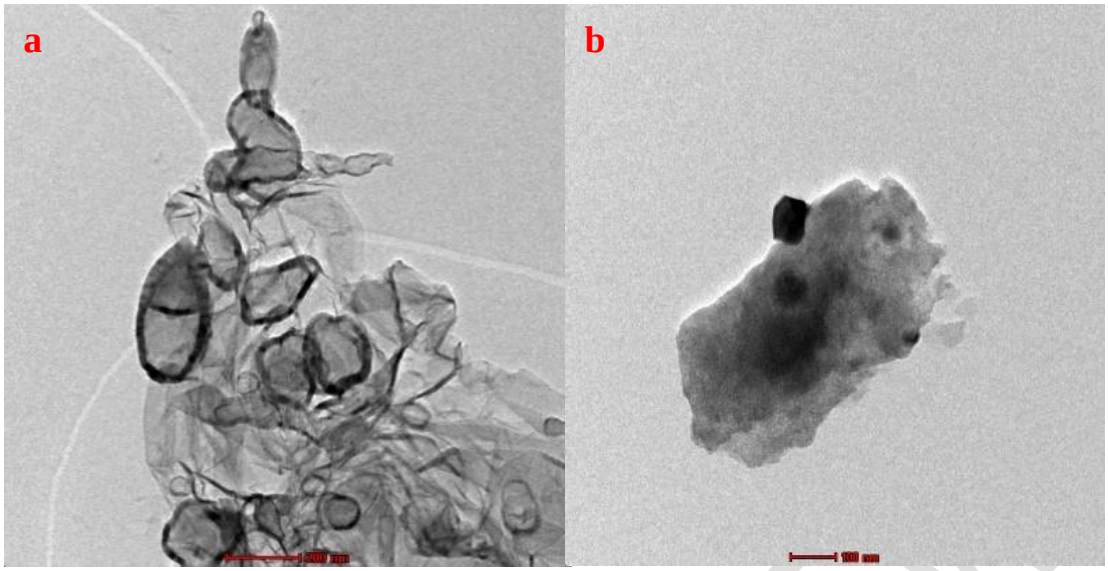


Figure 3. TEM images of GO (a) 200nm (b) 100nm

TEM images of graphene oxide (Figure.3) shows the wrinkles and folds (Jiang et al., 2020) (Javed et al., 2022), layered structure (Yoo et al., 2014), isolated sheets, nano-scale dimensions (Luo et al., 2019), contrast variations, dark spots and dots (Kolmakov et al., 2011). Wrinkles and folds are often exhibited by GO due to the presence of oxygen functional groups which confirms the amorphous nature. Contrast variations are due to the differences in the number of layers, defects and distribution of oxygen functional groups.

3.4. XRD

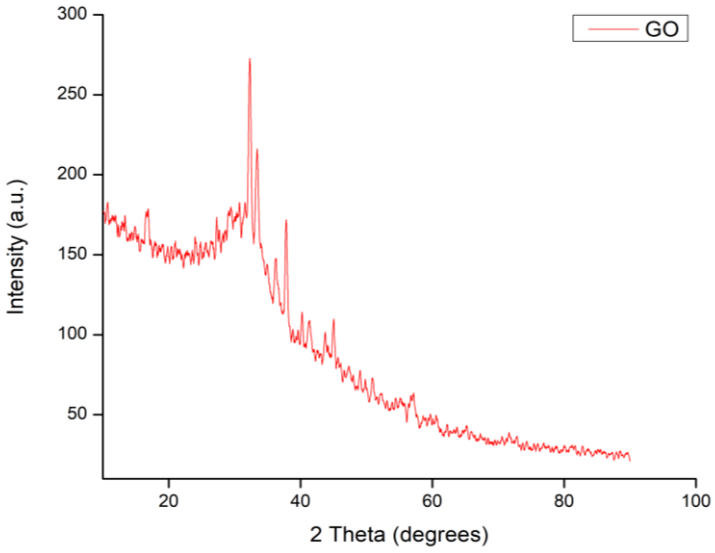


Figure 4. XRD pattern of GO

XRD diffractogram of GO reveals (Fig. 4) its amorphous structure but still displays peaks at 2Θ of 10.55, 16.77, 31.92.03, 37.91, 45.35 and 56.74. These peaks typically show the presence of both GO (10.55) and reduced graphene oxide (rGO) (31.92) phases in this sample. The amorphous nature of the precursor material (CF) used in the synthesis, as well as the vibrations in oxidation degree that take place during the synthesis process, may contribute to the shift in the diffraction pattern of the GO material. Primarily 2Θ of 10.55 degrees provides information on the interlayer d spacing of 0.84nm (Babaahmadi, 2023) with confirmation of the presence of GO sheets.

4. Conclusion

The characterization results collectively confirm the successful synthesis of GO nanoparticles from coconut frond waste. The GO samples exhibited a monodisperse distribution in colloidal form, distinct optical characteristics in the UV-VIS spectrum, and structural features consistent with GO's amorphous nature. Additionally, the presence of both GO and rGO phases was indicated by XRD analysis. This research holds promise for sustainable and cost-effective graphene oxide production from agricultural waste materials, opening up possibilities for various applications in nanotechnology and material science. Further studies may focus on optimizing the synthesis process and exploring potential applications of these GO nanoparticles.

References:

Al-Maliki, R. M., Alsalhy, Q. F., Al-Jubouri, S., Salih, I. K., AbdulRazak, A. A., Shehab, M. A., Németh, Z., & Hernadi, K. (2022). Classification of nanomaterials and the effect of graphene oxide (GO) and recently developed nanoparticles on the ultrafiltration membrane and their applications: A review. *Membranes*, *12*(11), 1043.

Alam, S. N., Sharma, N., & Kumar, L. (2017). Synthesis of graphene oxide (GO) by modified hummers method and its thermal reduction to obtain reduced graphene oxide (rGO). *Graphene*, *6*(1), 1-18.

Aziz, N. M., Shariff, A., Abdullah, N., & Noor, N. M. (2018). Characteristics of coconut frond as a potential feedstock for biochar via slow pyrolysis. *Malays J Fundam Appl Sci*, *14*(4), 408-413.

Babaahmadi, V. (2023). High durable three- dimensional electroconductive patterns on textiles: Direct laser scribing of crosslinked graphene oxide sheets. *Journal of Applied Polymer Science*, e53726.

Faisal, R., Putri, H. O., Sormin, A. Y., & Chafidz, A. (2020). Utilization of Coconut Fronds as Raw Material for Making Art Paper. Journal of Physics: Conference Series,

Grace, A. S., & Malar, G. P. L. (2020). Synthesis and characterization of graphene oxide from coconut husk ash. *Oriental journal of chemistry*, *36*(2), 348.

Guerrero-Contreras, J., & Caballero-Briones, F. (2015). Graphene oxide powders with different oxidation degree, prepared by synthesis variations of the Hummers method. *Materials Chemistry and Physics*, *153*, 209-220.

Guo, S., Garaj, S., Bianco, A., & Ménard-Moyon, C. (2022). Controlling covalent chemistry on graphene oxide. *Nature Reviews Physics*, *4*(4), 247-262.

Ibrahim, S., Hasaruddin, H., Hussin, W. M., & Ahmad, W. M. (2014). Durability of coconut fronds as attractors for fish aggregating devices (FADs): an observation based on leaf epidermis structure. *Aquaculture, Aquarium, Conservation & Legislation*, *7*(3), 225-233.

Kolmakov, A., Dikin, D. A., Cote, L. J., Huang, J., Abyaneh, M. K., Amati, M., Gregoratti, L., Günther, S., & Kiskinova, M. (2011). Graphene oxide windows for in situ environmental cell photoelectron spectroscopy. *Nature nanotechnology*, *6*(10), 651-657.

Luo, D., Zhang, F., Ren, Z., Ren, W., Yu, L., Jiang, L., Ren, B., Wang, L., Wang, Z., & Yu, Y. (2019). An improved method to synthesize nanoscale graphene oxide using much less acid. *Materials Today Physics*, *9*, 100097.

Macht, F., Eusterhues, K., Pronk, G. J., & Totsche, K. U. (2011). Specific surface area of clay minerals: Comparison between atomic force microscopy measurements and bulk-gas (N2) and-liquid (EGME) adsorption methods. *Applied Clay Science*, *53*(1), 20-26.

Sellathurai, A. J., Mypati, S., Kontopoulou, M., & Barz, D. P. (2023). High yields of graphene nanoplatelets by liquid phase exfoliation using graphene oxide as a stabilizer. *Chemical Engineering Journal*, *451*, 138365.

Shahriary, L., & Athawale, A. A. (2014). Graphene oxide synthesized by using modified hummers approach. *Int. J. Renew. Energy Environ. Eng*, *2*(01), 58-63.

Sharmila Rahale, C. (2010). Nutrient release pattern of nano–fertilizer formulations. In: Tamil Nadu Agricultural University Coimbatore.

Shinde, R., Shahi, D. K., Mahapatra, P., Singh, C. S., Naik, S. K., Thombare, N., & Singh, A. K. (2022). Management of crop residues with special reference to the on-farm utilization methods: A review. *Industrial Crops and Products*, *181*, 114772.