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Biosynthesis of Graphene Oxide Nanoparticles from Coconut Fronds

G. Kaviyarasan [a++*], C. Sharmila Rahale [b++], R. Shanmugasundaram [a], V. Palaniselvam [c] and N. Saranya [d]

[a] Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu, India.
[b] Centre for Agricultural Nanotechnology, Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu, India.
[c] Department of Renewable Energy Engineering, Agricultural Engineering College and Research Institute, Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu, India.
[d] Department of Plant Molecular Biology & Bioinformatics, Centre for Plant Molecular Biology and Biotechnology, Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu, India.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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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

[++]Directorate of Natural Resource Management;
**Corresponding author: E-mail: kaviyarasang2000@gmail.com;*

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 at 10.33° and 32.35° shown the interlayer spacing of 3.72 and 1.11 nm respectively. 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 unique properties of GO are utilized for water purification, oil spill cleanup, energy storage, sensors, composite materials, photodetectors, anticorrosive coatings, and so on. 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} [1] when its reduced to nano by ball milling will have 750 m^2g^{-1} [2]. "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 [3]. Sugarcane leaves [4], rice husk ash [5], coconut shell [6] & [7], oil palm empty fruit bunches [8], tea waste biomass [9], coconut coir dusts [10], sugarcane baggase [11] were some of the agricultural wastes been utilized for the synthesis of graphene oxide (GO).

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 [12] promising material for biochar [13], fish aggregation system attractants [14], 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 (GO).

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 [15,16]. It has oxygen-containing groups on the surface, such as epoxide, carbonyl, carboxyl, and hydroxyl which makes it has dispersible in water [17] 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 [6,18,19,20]. The main objective of this work is to utilize the final waste of coconut fronds for the synthesis of GO. 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 such as composite materials, water purification, oil spill cleanup, energy storage,

sensors, photodetectors, anticorrosive coatings, and several studies can be conducted in future.

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 0.1 M HCl and 0.1 M 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), which eliminates the particles greater than 74.5 µm [21].

2.2.2 Alkali activation

Freshly prepared 50 ml of 2M NaOH was added to 5g of sieved carbonized sample [22] 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

Modified Hummers method [6,18,20] was used to fabricate GO from the prepared carbonized sample. The activated carbon powder (1 g) and $NaNO_3$ (0.5 g) were added to a 250 ml 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 250 rpm in a Magnetic stirrer for an hour. This was followed by slow addition of $KMnO_4$ (3 g) 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 (50 ml) 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 100 ml deionized water, terminates the further oxidation and stirred for 30mins followed by the addition of 30% H_2O_2 to eliminate excess $KMnO_4$ [21] 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 forms cavitation process [23] which helps graphite oxide to exfoliate into graphene oxide and also helps in dispersion and size reduction of GO nanoparticles [24]. It was followed by centrifugation (5000 rpm for 15 mins) with distilled water for several washes which effectively eliminated the remaining acids to bring the solution to neutral pH and also remove contaminants from the solution along with the unexfoliated nanoparticles [25]. 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 (Horriba Scientific Nanopartica SZ-100, Japan), powder X-Ray Diffraction (Bruker D8 Advance X-Ray Diffractometer, Germany), UV-Vis Spectroscopy (SPECORD 210 PLUS – 223F1427) and Transmission Electron Microscope (FEI TECHNAI G-2, Netherlands).

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

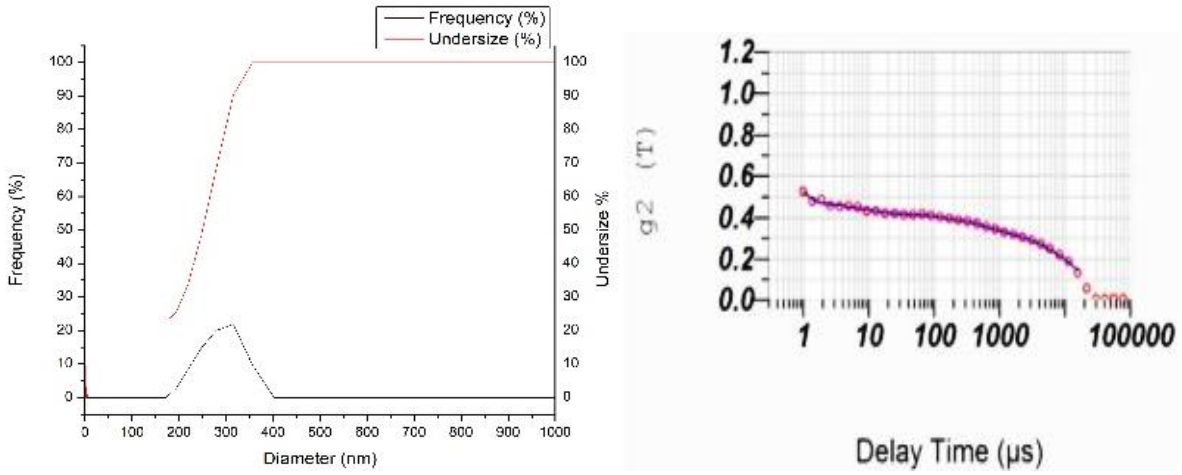

Fig. 1. PSA of GO (Solution)

The size distribution histogram of GO sheets in solution, is depicted Fig. 1. The histogram reveals, a predominantly monodisperse distribution [26] 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 [27]. 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

The optical characteristics of GO was determined using UV-Visible Spectroscopy (Hasani et al 2018). The spectrum of absorbance is shown in Fig. 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 at optical band gap of 2.2 eV [28]. The absorption spectrum reveals a prominent absorption peak at 234 nanometers. This peak corresponds to the π-π* electronic transitions in the GO sheets [29].

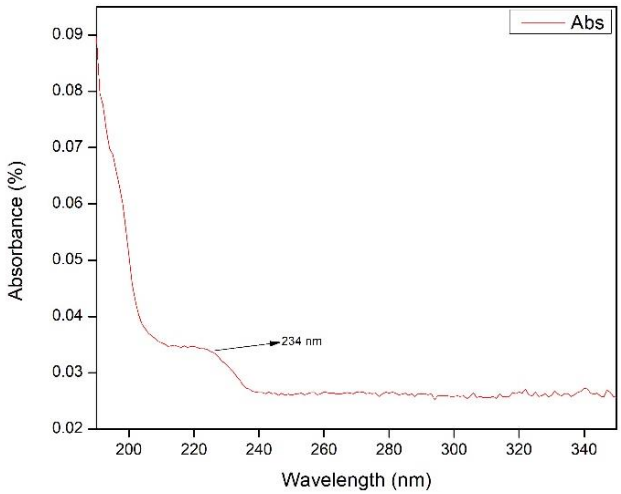

Fig. 2. UV-VIS spectrum of GO (Solution)

3.3 Transmission Electron Microscopy

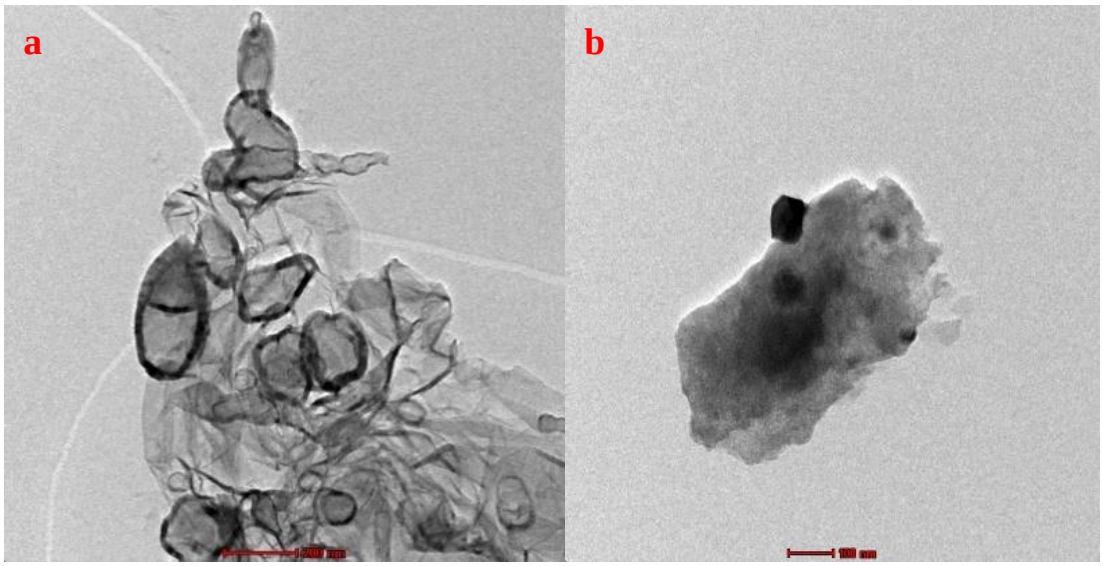

Fig. 3. TEM images of GO (a) 200 nm (b) 100 nm

TEM images of graphene oxide taken in FEI TECHNAI G-2, Netherlands (Fig. 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 [30], contrast variations, dark spots and dots [31]. 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

XRD diffractogram carried out on Bruker D8 Advance X-Ray Diffractometer, Germany with Cu Kα radiation (λ= 0.15418 nm) of GO reveals (Fig. 4) its amorphous structure but still displays peaks at 2Θ of 10.33°, 16.92°, 32.35°, 33.53° and

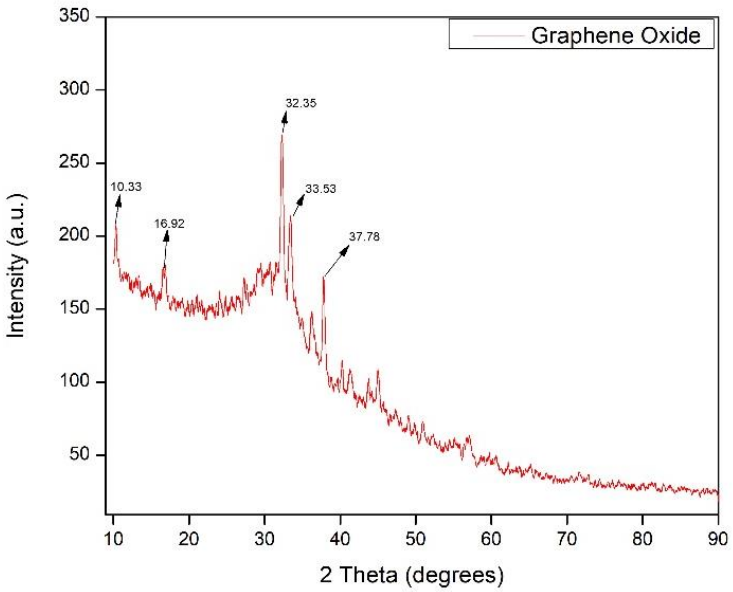

Fig. 4. XRD pattern of graphene oxide

Table 1.

Two thetas (deg)	FWHM (deg)	Intensity (Counts)	Height (Counts)	Grain size (nm)
10.33	2.238	206.84	154.0658	3.72
16.92	29.469	179.64	102.6002	0.28
32.35	7.8143	269.06	69.4432	1.11
33.53	39.4314	212.99	74.332	0.22
37.78	1.7469	172.02	-27.7421	5.02

37.78°. These peaks typically show the presence of both GO (10.33°) [32] and reduced graphene oxide (rGO) (32.35°) 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 10.33° and 32.35° provides information on the interlayer d spacing of 3.72 nm and 1.11 nm for GO and rGO respectively [32,33] with confirmation of the presence of GO and rGO.

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 [26], distinct optical characteristics showing π-π^* electronic transitions in the GO sheets by UV-VIS spectrum analysis [29], and structural features consistent with GO's amorphous nature. Additionally, the presence of both GO and rGO phases was indicated by the peak shown in 10.33° and 32.35° respectively by XRD analysis [32]. 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.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Macht F, Eusterhues K, Pronk GJ, Totsche KU. Specific surface area of clay minerals: Comparison between atomic force microscopy measurements and bulk-gas (N2) and-liquid (EGME) adsorption methods. Applied Clay Science. 2011; 53(1):20-26.
2. Sharmila Rahale C. Nutrient release pattern of nano–fertilizer formulations. In: Tamil Nadu Agricultural University Coimbatore; 2010.
3. Shinde R, Shahi DK, Mahapatra P, Singh CS, Naik SK, Thombare N, Singh AK. Management of crop residues with special reference to the on-farm utilization methods: A review. Industrial Crops and Products. 2022;181:114772.
4. Thangaraj B, Mumtaz F, Abbas Y, Anjum DH, Solomon PR, Hassan J. Synthesis of Graphene Oxide from Sugarcane Dry Leaves by Two-Stage Pyrolysis. Molecules. 2023;28(8):3329.
5. Zhang TY, Liou TH, Chiu SE, Hsu CC, Liu WY. A sustainable route for production of graphene oxide-contained nanostructured carbons from rice husk waste and its application in wastewater treatment. Environmental Technology & Innovation. 2023;32:103270.
6. Ariyanti D, Lesdantina D, Purbasari A, Astuti Y. Synthesis of graphene-like material derived from biomass from agricultural waste and its application in Cu (II) removal. Korean Journal of Chemical Engineering. 2023;40(4):964-974.
7. Nanda R. Structure Analysis of Graphene Micro Oxide from Old Coconut Shell Waste. Pillar of Physics. 2022;15(1).
8. Ramli R, Hidayat R. Graphene Oxide Based on Biomass Waste: Synthesis and Applications; 2023.
9. Faiz MA, Azurahanim CC, Yazid Y, Suriani AB, Ain MSN. Preparation and characterization of graphene oxide from tea waste and it's photocatalytic application of TiO2/graphene nanocomposite. Materials Research Express. 2020;7(1):015613.
10. Supriadi CP, Kartini E, Honggowiranto W, Basuki KT. Synthesis and characterization

of carbon material obtained from coconut coir dust by hydrothermal and pyrolytic processes. International Journal of Technology. 2017;8(8):1470-1478.
11. Somanathan T, Prasad K, Ostrikov K, Saravanan A, Mohana Krishna V. Graphene oxide synthesis from agro waste. Nanomaterials. 2015;5(2):826-834.
12. Faisal R, Putri HO, Sormin AY, Chafidz A. Utilization of coconut fronds as raw material for making art paper. Journal of Physics: Conference Series; 2020.
13. Aziz NM, Shariff A, Abdullah N, Noor NM. Characteristics of coconut frond as a potential feedstock for biochar via slow pyrolysis. Malays J Fundam Appl Sci. 2018;14(4):408-413.
14. Ibrahim S, Hasaruddin H, Hussin WM, Ahmad WM. Durability of coconut fronds as attractors for fish aggregating devices (FADs): An observation based on leaf epidermis structure. Aquaculture, Aquarium, Conservation & Legislation. 2014;7(3):225-233.
15. Alam SN, Sharma N, Kumar L. Synthesis of graphene oxide (GO) by modified hummers method and its thermal reduction to obtain reduced graphene oxide (rGO). Graphene. 2017;6(1):1-18.
16. Guerrero-Contreras J, Caballero-Briones F. Graphene oxide powders with different oxidation degree, prepared by synthesis variations of the Hummers method. Materials Chemistry and Physics. 2015; 153:209-220.
17. Al-Maliki RM, Alsalhy QF, Al-Jubouri S, Salih IK, AbdulRazak AA, Shehab MA, Németh Z, Hernadi K. Classification of nanomaterials and the effect of graphene oxide (GO) and recently developed nanoparticles on the ultrafiltration membrane and their applications: A review. Membranes. 2022;12(11):1043.
18. Omar H, Malek N, Nurfazianawatie M, Rosman N, Bunyamin I, Abdullah S, et al. A review of synthesis graphene oxide from natural carbon based coconut waste by Hummer's method. Materials Today: Proceedings; 2022.
19. Shahriary L, Athawale AA. Graphene oxide synthesized by using modified hummers approach. Int. J. Renew. Energy Environ. Eng. 2014;2(01):58-63.
20. Supriyanto G, Rukman NK, Nisa AK, Jannatin M, Piere B, Abdullah A, et al. Graphene oxide from Indonesian biomass: Synthesis and characterization. Bio Resources. 2018;13(3):4832-4840.
21. Sujiono EH, Zabrian D, Dahlan M, Amin B, Agus J. Graphene oxide based coconut shell waste: Synthesis by modified Hummers method and characterization. Heliyon. 2020;6(8).
22. Grace AS, Malar GPL. Synthesis and characterization of graphene oxide from coconut husk ash. Oriental Journal of Chemistry. 2020;36(2):348.
23. Marcano DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, Slesarev A, et al. Improved synthesis of graphene oxide. ACS Nano. 2010;4(8):4806-4814.
24. Panatarani C, Maulana AO, Rianto A, Joni I. Preparation of graphite oxide by sodium cholate intercalation and sonication from Indonesian natural graphite. AIP Conference Proceedings; 2016.
25. Chen J, Yao B, Li C, Shi G. An improved Hummers method for eco-friendly synthesis of graphene oxide. Carbon. 2013;64:225-229.
26. Baweja H, Jeet K. Economical and green synthesis of graphene and carbon quantum dots from agricultural waste. Materials Research Express. 2019;6(8): 0850g0858.
27. Guo S, Garaj S, Bianco A, Ménard-Moyon C. Controlling covalent chemistry on graphene oxide. Nature Reviews Physics. 2022;4(4):247-262.
28. Abid Sehrawat P, Islam S, Mishra P, Ahmad S. Reduced graphene oxide (rGO) based wideband optical sensor and the role of Temperature, Defect States and Quantum Efficiency. Scientific Reports. 2018;8(1):3537.
29. Sellathurai AJ, Mypati S, Kontopoulou M, Barz DP. High yields of graphene nanoplatelets by liquid phase exfoliation using graphene oxide as a stabilizer. Chemical Engineering Journal. 2023;451: 138365.
30. Luo D, Zhang F, Ren Z, Ren W, Yu L, Jiang L, et al. An improved method to synthesize nanoscale graphene oxide using much less acid. Materials Today Physics. 2019;9:100097.
31. Kolmakov A, Dikin DA, Cote LJ, Huang J, Abyaneh MK, Amati M, et al. Graphene oxide windows for in situ environmental cell photoelectron spectroscopy. Nature Nanotechnology. 2011;6(10):651-657.
32. Siaw W, Tsuji T, Manaf NA, Patah MA, Jan BM. Synthesis of graphene oxide from

industrial waste. IOP Conference Series: Materials Science and Engineering; 2020.
33. Babaahmadi V. High durable three-dimensional electroconductive patterns on textiles: Direct laser scribing of crosslinked graphene oxide sheets. Journal of Applied Polymer Science. 2023;e53726.

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