
ENHANCING THE CAPACITANCE PERFORMANCE OF REDUCED GRAPHENE OXIDE BY GUINEA FOWL FEATHER DERIVED NITROGEN DOPING

Abdu M. Ali¹, Salisu Nasir², M. B. Idris², Naziru Shu'aibu¹ and Mustapha Isah^{1*}

¹Department of Chemistry, Jigawa State College of Education, Gumel

²Department of Chemistry, Federal University, Dutse.

*Email: abuabdallah99@mail.com

Abstract

The reason behind this research is to enhance the capacitance performance of reduced graphene oxide (rGO) through nitrogen doping derived from Guinea fowl feathers. The large surface area of rGO area and its electrical conductivity explain its suitability for super capacitor electrodes, while nitrogen doping introduces additional active sites and improves electron transfer. This research reports effectiveness of Guinea fowl feather in simultaneously reducing and nitrogen doping. Graphene oxide was reduced, after its synthesis by modified Hummer's method, by hydrothermal method with and without the Guinea fowl feather and labelled as N-rGO and rGO respectively. The impact of the guinea fowl feather derived nitrogen doping on the morphology and textual properties of the rGO was studied using XRD, FTIR and TEM. On the other hand, the electrochemical performance of the N-doped rGO was studied using Galvanostatic Charge Discharge (GCD) and Cyclic Voltammetry (CV), respectively. The dopant overcomes the restacking of graphene layers, leading to mesopores and more surface area available for electron movement and better electrochemical performance. The Faradaic behaviour of the dopant makes N-rGO_{2.5} exhibit higher specific capacitance (216Fg⁻¹ and 156Fg⁻¹) than the undoped rGO (95.6Fg⁻¹) in aqueous 0.5M H₂SO₄ electrolyte.

Keywords: Graphene oxide, Guinea fowl, Hummer's method, Doping, Super Capacitance

1.0 Introduction

The global energy landscape confronts challenges from population growth, urbanization, and environmental concerns, emphasizing the need for sustainable and accessible energy sources. Fossil fuel reliance contributes to pollution and climate change, underscoring the urgency of transitioning to renewables [1]. Limited access to modern energy services impedes socio-economic development, and inefficient energy use persists, highlighting the importance of energy-efficient technologies [2].

Renewable energy sources like solar and wind power are crucial for reducing carbon emissions. Effective energy storage, facilitated by devices such as fuel cells, batteries, and super capacitors, is essential due to the intermittent nature of renewables. Super capacitors, with attributes like high power density, rapid charge-discharge capabilities, long cycle life, portability, and safety, have garnered significant interest [3]. They hold the potential to bridge the energy/power density gap between batteries and capacitors, offering higher power density than the latter and greater energy density than the former [4]. However, a notable drawback of super capacitors is their lower storage capacity compared to batteries. Research has focused on discovering new materials for super capacitor electrodes with improved capacity. Activated carbon is a prominent electrode material due to its high specific surface area and cost-effectiveness [5]. Carbon-based super capacitors store energy through the electrochemical double-layer capacitance mechanism, accumulating charge at the electrode-electrolyte interfaces. While carbon-based electrochemical double-layer capacitors (EDLCs) offer high cyclic stability and prolonged service life, they face a limitation in specific capacitance, around 150Fg^{-1} . Consequently, their energy density, approximately 5Whkg^{-1} , is lower than batteries like lead-acid batteries with an energy density of around 40Whkg^{-1} [6].

The quest for efficient energy storage solutions is paramount in today's technology-driven world, with super capacitors playing a crucial role due to their high power density, rapid charge-discharge capabilities, and long cycle life. Reduced graphene oxide (rGO) has emerged as a promising material for super capacitor electrodes, owing to its large surface area, excellent electrical conductivity, and robust mechanical strength [7]. However, to maximize its potential, further enhancements in its electrochemical performance are necessary.

Nitrogen doping has been identified as an effective strategy to improve the capacitance performance of rGO. By introducing nitrogen atoms into the carbon lattice of rGO, additional active sites are created, which facilitate enhanced charge storage and improve electron transfer efficiency [8]. This modification not only increases the specific capacitance but also boosts the overall energy and power density of the super capacitor.

Guinea fowl feathers, an abundant and low-cost biomass waste, present a sustainable and environmentally friendly source of nitrogen for doping rGO. Rich in nitrogen-containing compounds such as keratin, chicken feathers can be converted into a nitrogen source through various chemical processes [7]. Utilizing this waste material not only provides a green approach to material synthesis but also addresses waste management issues.

Studies have demonstrated that nitrogen-doped rGO derived from Guinea fowl feathers exhibits superior electrochemical performance compared to undoped rGO. Specifically, nitrogen doping enhances the specific capacitance, energy density, and cycle stability of rGO-based super capacitors. For instance, nitrogen-doped rGO from hen feathers showed a significant increase in specific capacitance and excellent cycling stability over thousands of charge-discharge cycles [9].

This research aims at improving capacitive performance of rGO through Guinea fowl feathers derived nitrogen doping.

2.0 Material and Method

The first stage involves purchasing of graphite powder and collection of waste chicken feathers from chicken selling points in Gumel local government.

2.1 Synthesis of Graphene Oxide

Graphene oxide was produced through an adjusted approach based on Hummer's technique, originally developed in 1958. Initially, 1g of graphite powder was weighed and transferred into a 500mL round-bottom flask holding 50mL of concentrated sulphuric acid (98%). The flask was immersed in an ice bath and affixed to a magnetic stirrer. Subsequently, 1g of sodium nitrate (NaNO_3) was introduced into the solution, followed by continuous stirring for 2 hours while keeping the temperature between 0 and 5°C. Gradually, 6g of potassium permanganate (KMnO_4) was incorporated into the suspension, ensuring the temperature remained under 15°C. After complete addition, the ice bath was removed, and the mixture was stirred at ambient temperature for 48 hours, resulting in a brown, paste-like consistency. To dilute the reaction mixture, 50mL of distilled water was added drop wise, triggering a rapid temperature rise to approximately 98°C, alongside effervescence and a deepening brown hue. A further 100mL of distilled water was introduced to sustain stirring. The reaction was terminated by adding 10 mL of hydrogen peroxide (H_2O_2), which induced a colour shift to yellow, indicating successful graphene oxide formation. Purification involved treating the product with 10% hydrochloric acid (HCl), followed by triple centrifugation. Deionized water was added repeatedly until a neutral pH of 7 was attained. Lastly, the gel-like material was oven-dried at 60°C for 6 hours to yield the final graphene oxide product.

2.2 Pretreatment of the Feathers

Chicken feathers obtained from a processing plant undergo a 24-hour ether soaking to remove stains, oils, and grease. Following this, the feathers are washed with soapy water, sun-dried, blended, and stored in a sealed plastic bag.

2.3 Dissolving of Chicken Feathers

In a 2L conical flask, a 0.5M sodium sulphite solution was prepared. 50g of blended chicken feathers was added to the solution, which was then heated to 30°C. The pH was kept between 10-13, and the mixture was continuously stirred for 6 hours. Afterward, the solution was filtered and centrifuged at 10,000rpm for 5 minutes. The resulting supernatant was meticulously collected and further filtered using filter paper to eliminate particles.

2.4 Synthesis of Reduced Graphene Oxide and Nitrogen-doped Reduced Graphene Oxide

Typically, 160 mg of GO was dispersed in 60 mL of distilled water by sonication. Then various amounts of the chicken feather extract (2.0 mL, 2.5 mL and 3.0 mL) were added to the dispersions in batches and stirred for 30 minutes. Subsequently, each batch was transferred into the Teflon-lined hydrothermal autoclave and heated at 180 °C for 12 hours. The content was then allowed to naturally cool down to room temperature. The black products were taken out and washed with distilled water, followed by ethanol and then dried for 12 hours at 60 °C. The products were the nitrogen doped reduced graphene oxide.

Similarly, undoped reduced graphene oxide was prepared in the absence of the chicken feather extract.

2.5 Physicochemical Characterization

2.5.1 Fourier Transform Infrared Spectroscopy (FTIR)

This was used to analyze functional groups present on the surface of the as-synthesized N-rGO.

2.5.2 Transmission Electron Microscopy (TEM):

This High-resolution imaging technique was used for visualizing the morphology and structure of N-rGO. It is useful for observing the Nano scale structure and confirming the reduction.

2.5.3 X-ray Diffraction (XRD)

XRD was employed to examine the crystal structure and purity of N-rGO. This non-destructive technique is utilized to discern phase purity, phase composition and crystallinity in the synthesized samples by analyzing their diffraction patterns. Bragg's law is applied to elucidate the diffraction pattern of the sample.

$$n\lambda = 2d\sin\theta$$

Then, Scherrer equation was used to calculate the crystallites sizes, given by:

$$D = 0.9\lambda/\beta \cos \theta$$

Where λ is the wavelength, D is the crystallites size, θ is the Bragg's angle and β is the full width half maximum of the most intense peak.

2.6 Electrochemical Characterization

2.6.1 Cyclic Voltammetry (CV)

Cyclic Voltammetry (CV) was employed for evaluating the electrochemical performance of the N-rGO electrode. This method includes sweeping the potential within specified limits at a controlled rate while simultaneously measuring the resulting current. CV offers valuable insights into the electrochemical capacitance and redox behavior of the N-rGO materials (Zhao *et al.*, 2016).

2.6.2 Galvanostatic Charge-Discharge (GCD)

This was utilized to assess the charge storage capacity and rate performance of the N-rGO-based super capacitors. In this method, a constant current is applied to the device and the voltage change over time is monitored. GCD curves provide insights into the specific capacitance and energy density of the electrode material [10].

3.0 Results and Discussion

The results from the different analysis were presented below;

3.1 Physicochemical Characterization

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra as presented in figure 1 revealed several characteristic peaks indicating the presence of key functional groups. The absorption band at approximately 2648cm^{-1} is suggestive of hydrogen-bonded $-\text{OH}$ or possibly thiol ($-\text{SH}$) groups, or even carboxylic acid dimers [11]. A notable peak at 2337.7cm^{-1} corresponds to the asymmetric stretching of carbon dioxide, often attributed to atmospheric CO_2 contamination or residual CO_2 trapped within the material [12]. The peak around 1564.4cm^{-1} is typically associated with $\text{C}=\text{C}$ stretching in aromatic structures or $\text{N}-\text{H}$ bending, indicating the presence of nitrogen-containing functionalities such as amines or pyridinic nitrogen, particularly in nitrogen-doped materials [13]. Additionally, the prominent peak at 1116.7cm^{-1} is attributed to $\text{C}-\text{O}$ stretching vibrations, which are characteristic of alcohols, ethers, or epoxy groups remaining from partial oxidation or reduction processes [14]. These findings confirm the presence of oxygen- and nitrogen-based surface functionalities, which are crucial for the chemical reactivity and performance of the material. However, as the nitrogen loading level increases, a slight band broadening is observed, although the absorption patterns remain similar.

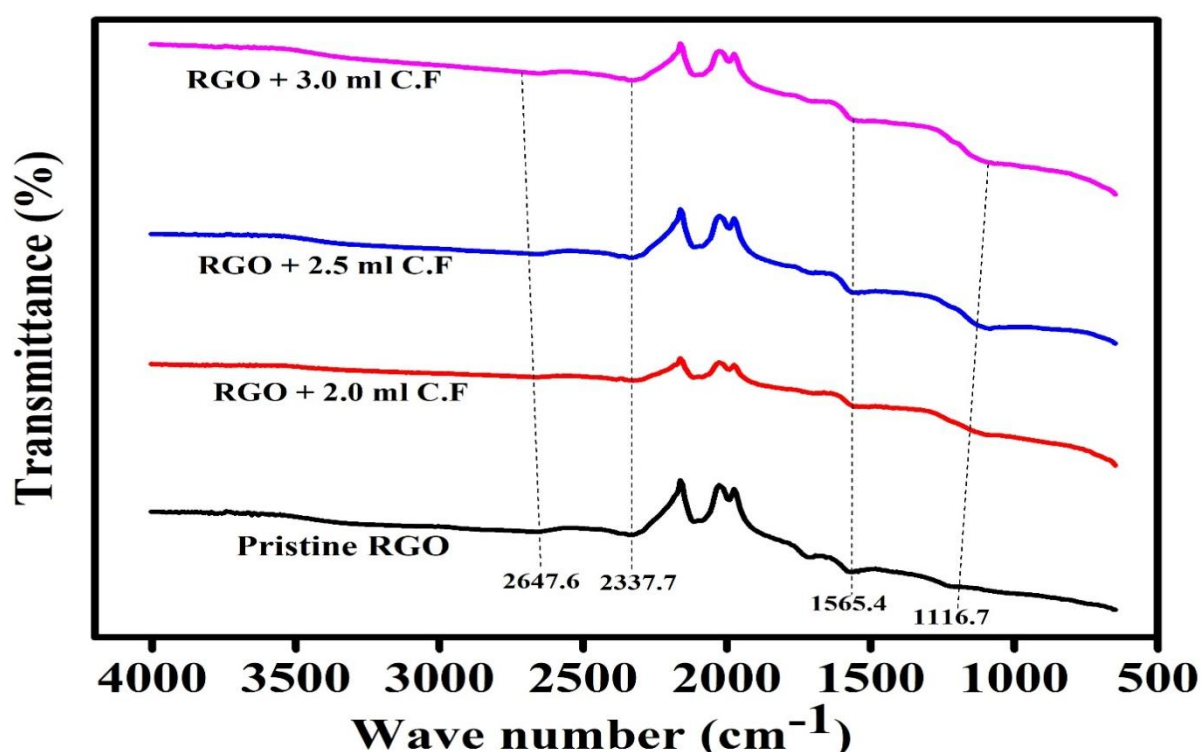


FIGURE 1: FTIR Spectra of rGO and N-rGO

Transmission Electron Microscopy (TEM):

The TEM micrographs of nitrogen-doped reduced graphene oxide (N-rGO) synthesised using varying volumes of chicken feather extract reveal a strong correlation between nitrogen loading, morphology, and electrochemical performance. At 2.0mL loading level (figure 2a & b), the N-rGO displays uniformly dispersed spherical nanoparticles with limited active sites, correlating with lower specific capacitance. Increasing the extract volume to 2.5mL (figure 2c & d) results in denser surface coverage and larger particle sizes, indicating optimal nitrogen

incorporation and enhanced capacitive behaviour, thereby improving capacitance performance [15] [16]. Overall, the 2.5mL nitrogen loading level presents the most favourable morphology for super capacitor applications.

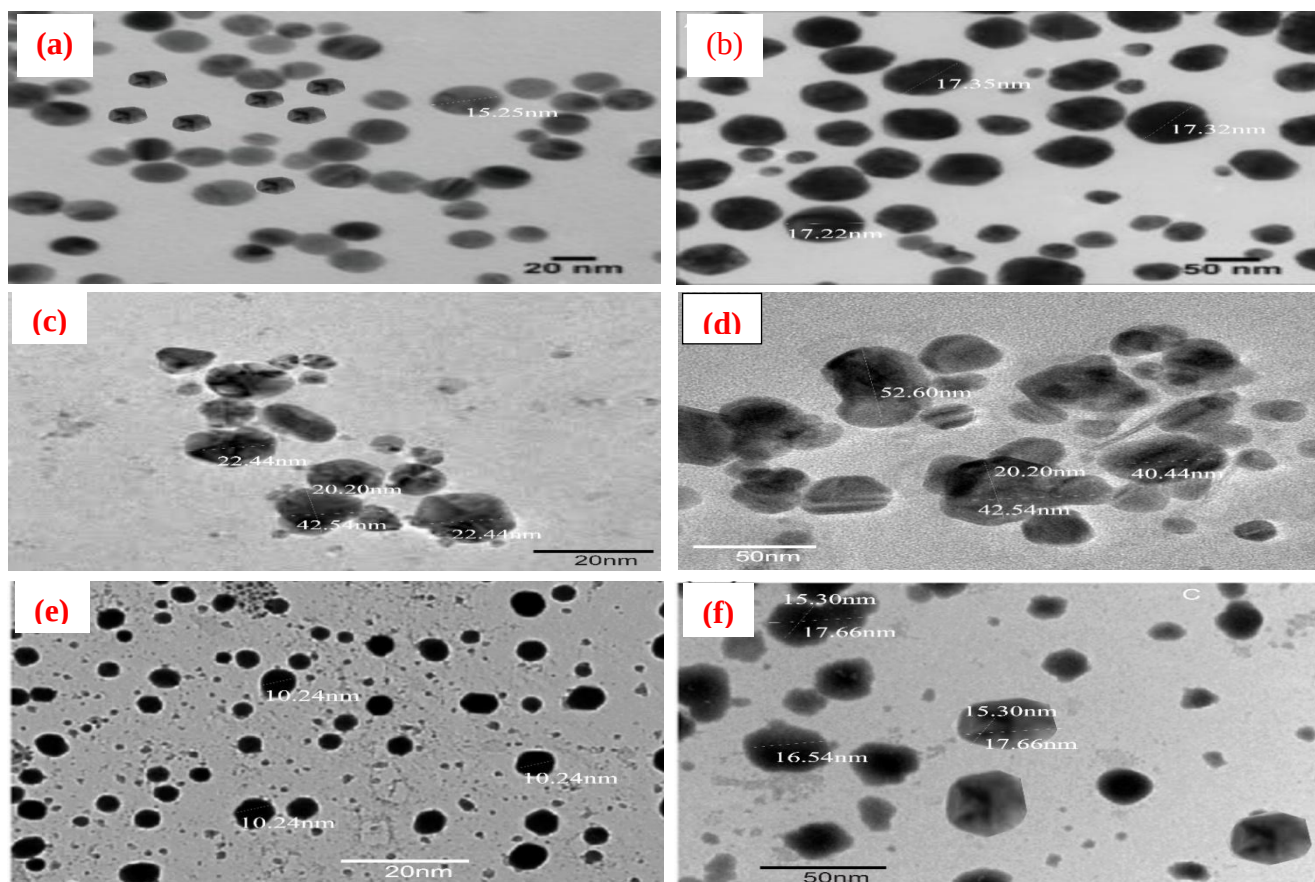


FIGURE 2: TEM Images of N-rGO at different magnifications

X-ray Diffraction (XRD)

The XRD spectra revealed key structural features indicative of the crystalline and partially disordered nature of the analysed carbon-based materials. A broad diffraction peak around $24\text{--}26^\circ 2\theta$ was consistently observed, corresponding to the (002) plane of graphitic carbon, suggesting the presence of disordered or turbostratic graphene layers typically found in reduced graphene oxide [17]. In some samples, notably in Figure (b), sharper peaks at higher angles such as 43° , 54° , and $77^\circ 2\theta$ were evident, which are attributable to the (100), (004), and (110) planes of hexagonal graphite, implying a higher degree of crystallinity [18]. Variations in peak positions and intensities across the figures indicate structural modifications, such as exfoliation, interlayer spacing changes, or heteroatom doping. These are commonly associated with chemical reduction or functionalisation processes, as suggested by shifts or reductions in the (002) peak intensity [19].

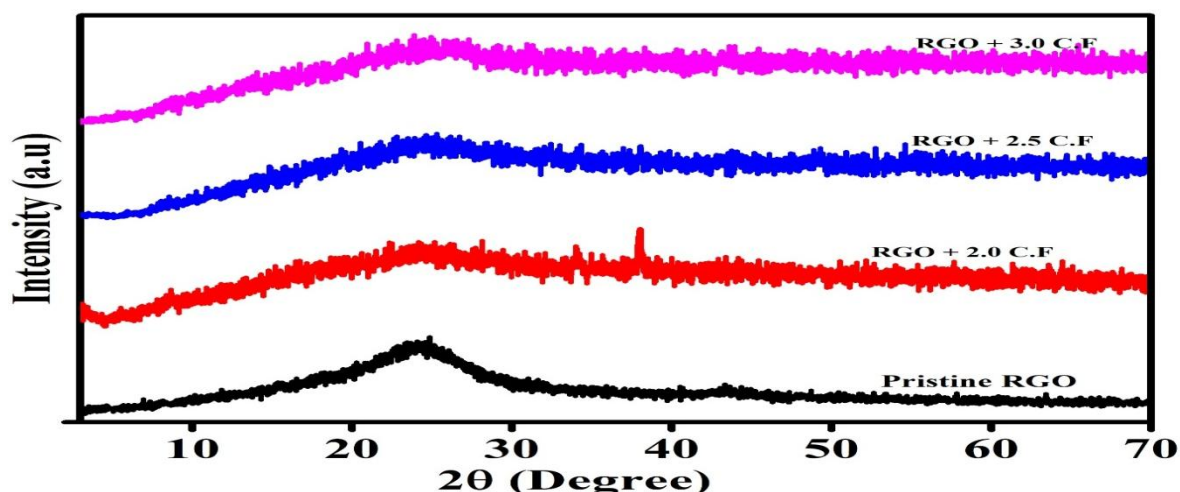


FIGURE 3: XRD Spectra of Pristine rGO and N-rGO

3.2 Electrochemical Characterization

Cyclic Voltammetry (CV)

The capacitive behaviour of both rGO and nitrogen-doped rGO (N-rGO) electrodes, each incorporating varying levels of nitrogen content, was investigated through cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD). The CV profiles of rGO and N-rGO, depicted in Figure 4a, reveal that the rGO exhibits a nearly rectangular shape, indicative of electric double-layer capacitance. In contrast, distinct redox peaks appear in the N-rGO curves, attributed to rapid Faradaic processes introduced by nitrogen doping, as shown in Figure 4b and 4c. Furthermore, the CV curve of N-rGO encloses a larger area compared to that of rGO, with the sample containing 2.5mL nitrogen loading level demonstrating the most extensive area. This increased area reflects the superior capacitance performance of N-rGO over pure rGO.

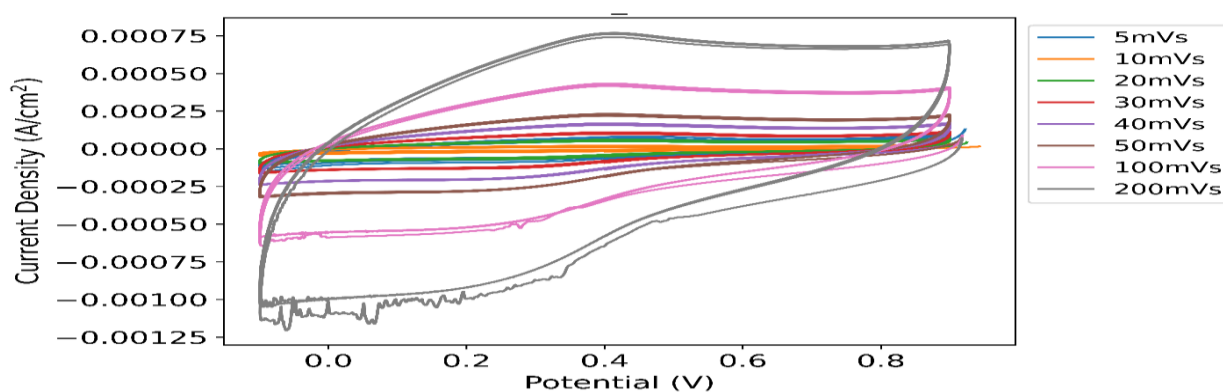


Figure 4a: Cyclic Voltammetry (CV) of rGO

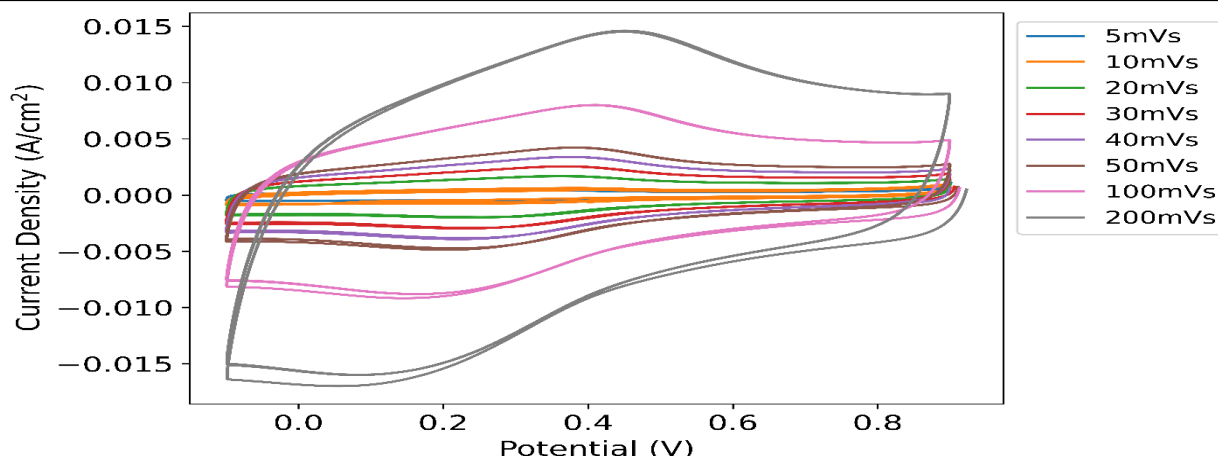


Figure 4b: Cyclic Voltammetry (CV) at 2.0mL

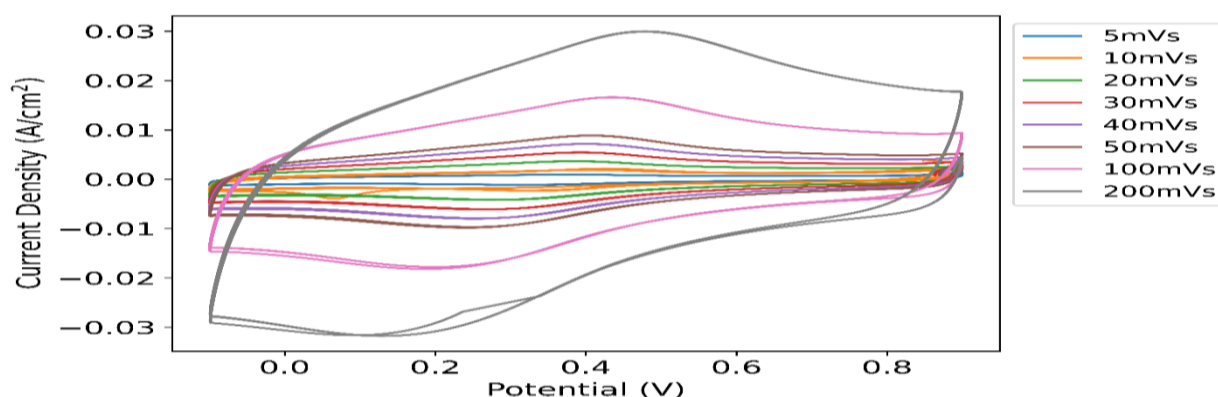


Figure 4c: Cyclic Voltammetry (CV) at 2.5mL

Galvanostatic Charge Discharge (GCD)

Galvanostatic charge-discharge (GCD) measurements were conducted to assess the electrochemical properties of both rGO and nitrogen-doped reduced graphene oxide (N-rGOx) samples. These measurements were performed across a range of current densities, from 0.5 Ag^{-1} to 20 Ag^{-1} . It was observed that, for all materials, the duration of the charge-discharge cycles decreased as the current density increased. However, at any specific current density, the N-rGOx samples exhibited longer charge-discharge durations compared to pristine rGO. Among them, N-rGO2.5 demonstrated the most prolonged charge and discharge times, indicating its superior charge storage capability relative to the other samples. The order of charge storage capacity is as follows: $\text{N-rGO2.5} > \text{N-rGO2.0} > \text{rGO}$.

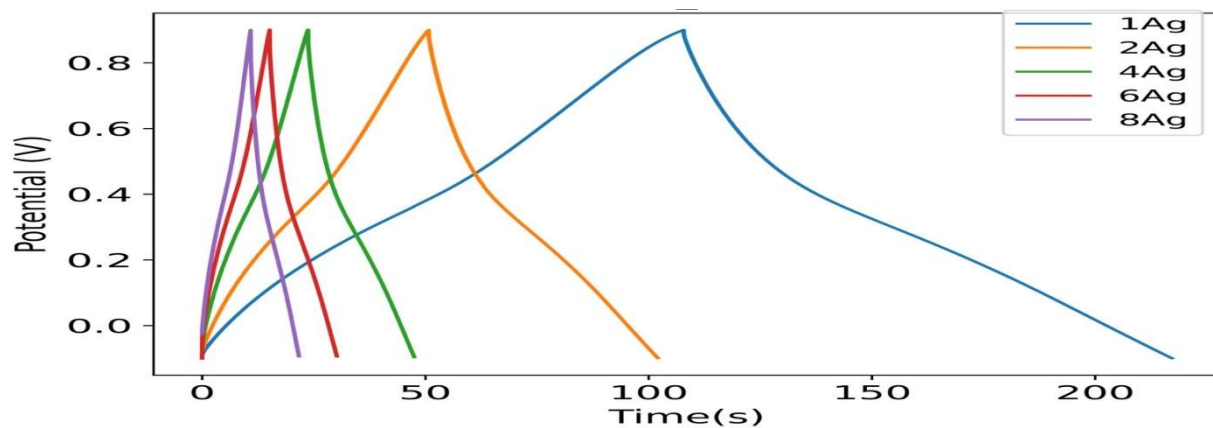


Figure 5a: Galvanostatic Charge Discharge (GCD) of rGO

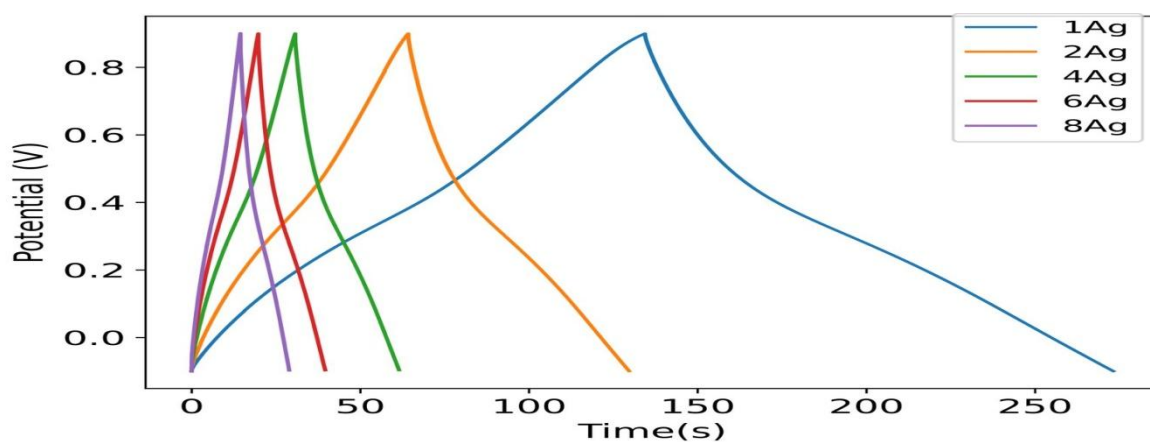


Figure 5b: Galvanostatic Charge Discharge (GCD) at 2.0mL

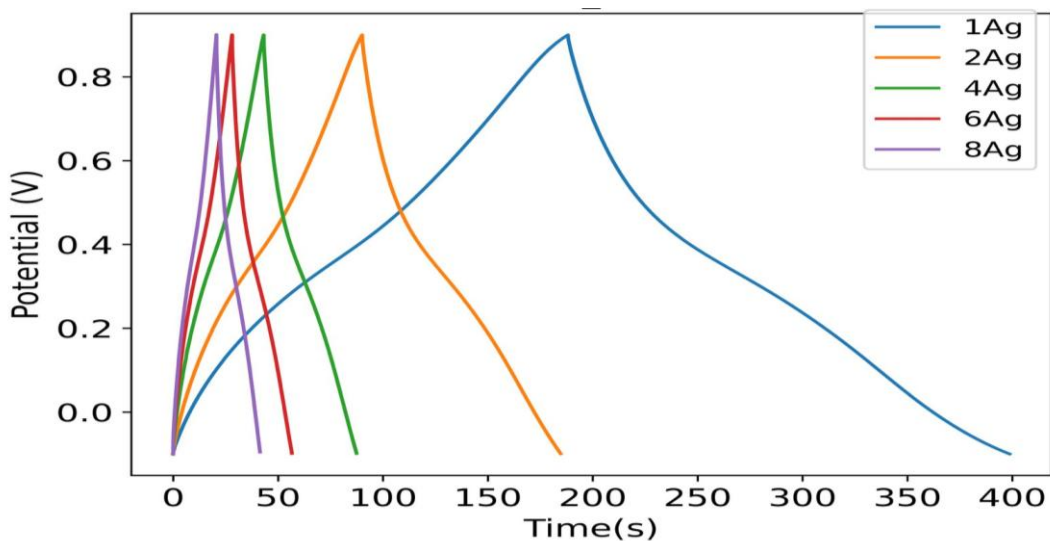


Figure 5c: Galvanostatic Charge Discharge (GCD) at 2.5mL

Table 1: Comparison of Capacitance Properties of rGO and N-rGO_x Materials

Material	Guinea Fowl Feather Extract Volume (mL)	Electrolyte Used	Current Density (Ag ⁻¹)	Specific Capacitance (Fg ⁻¹)
N-rGO _{2.0}	2.0	0.5 M H ₂ SO ₄	0.5	157
N-rGO _{2.5}	2.5	0.5 M H ₂ SO ₄	0.5	216
Pristine rGO	0.0	0.5 M H ₂ SO ₄	0.5	95.6

The capacitance of reduced graphene oxide (rGO) significantly improved from 95.6 F g⁻¹ in its undoped state to a maximum of 216 F g⁻¹ when treated with a 2.5 mL nitrogen doping level. This result is consistent with the findings [20], who demonstrated through theoretical analysis that graphene electrodes featuring moderate pore sizes ranging from 4.2 to 10 Å promote effective electrolyte penetration and support superior rate performance. Furthermore, the incorporation of nitrogen atoms enhances charge storage by acting either as electron donors or proton acceptors, which contributes to increased pseudo capacitance.

Conclusion

This study has shown that nitrogen doping of reduced graphene oxide (rGO) using Guinea fowl feather extract significantly improves its electrochemical properties, thereby enhancing its suitability for super capacitance, higher charge storage capacity, and improved redox behavior compared to pristine rGO. Physicochemical analyses (FTIR, TEM and XRD) confirmed the effective incorporation of nitrogen in to the graphene framework and highlighted the structural and morphological modifications caused by optimal doping conditions. Electrochemical characterization further revealed that the sample prepared with 2.5mL of feather extract delivered the highest capacitance performance, attributed to the ideal balance between nitrogen content, porosity and surface area. These findings underline the potential of utilizing sustainable , biomass-derived nitrogen sources such as poultry feathers to enhance the performance of carbon-based electrode materials, resulting in a cost-effective and environmentally friendly route for the development energy storage devices of the generation to come.

References

- [1] "International Energy Agency," 2020. [Online]. Available: <https://www.iea.org/reports/world-energy-outlook-2020>.
- [2] "International Energy Agency," 2019. [Online]. Available: <https://www.iea.org/reports/world-energy-access-2019>.
- [3] Yu, A., Chabot, V. & Zhang, J., *Electrochemical Super capacitors for Energy Storage and Delivery: fundamentals and Applications*, CRC Press, 2013.
- [4] Lu, Y., Li, Y., Tong, Y. & Li, G., "Hybrid Nanonet/Nanoflake NiCo₃O₄ Electrodes with an Ultrahigh Surface Area for Super capacitors," *Journal of Solid State Electrochemistry*, 18, pp. 3143-3152, 2015.
- [5] Afif A., Zaini M. A. A., Azizi, M. F., Ismail, M. S. H. & Azmi, W. F. W., "Advanced Materials and Technologies for Hybrid Super capacitors for energy Storage," *Materials Today Energy*, 13, pp. 1-23, 2019.
- [6] Zhi, M., Xiang, C., Li, J., Li, M. & Wu, N., "Nanostructured Carbon-metal Oxide Composite Electrodes for Super capacitors: A Review," *Nanoscale*, 5(1), pp. 72-88, 2013.
- [7] Yu, L., Zhang, Y., Shi, H. & Fan, L., "Sustainable Nitrogen-doped Graphene from Biomass for High-Performance Super capacitors," *ACS sustainable Chemistry & Engineering*, 9(34), pp. 11434-11442, 2021.
- [8] Li, X., Wang, G. & Jiang, W., "Biomass-derived Nitrogen-doped Graphene for Super capacitors," *Materials Today Energy*, 18, pp. 100-123, 2020.
- [9] Yu, Z., Wang, L., Zhang, X. & Li, X., "Efficient Preparation of Biomass-based Mesoporous Carbons for Super capacitors with both High Energy Density and High Power Density," *Journal of Power Sources*, 240, pp. 109-113, 2021.
- [10] Meng, C., Liu, C., Chen, L., Hu, C. & Fan, S., "Sub-micrometer-thick all-solid-state Super capacitors with High Power and Energy Densities," *Advanced Materials*, 22(36), pp. 5315-5320, 2010.
- [11] Silverstein, R. M., Webster, F. X., Kiemle, D. J., & Bryce, D. L., *Spectrometric Identification of Organic Compounds*, CRC Press, 2015.
- [12] B. C. Smith, *Fundamentals of Fourier transform infrared spectroscopy introduction to spectroscopy* (5th ed.), Cengage Learning, 2011.
- [13] Pavia, D. L., Lampman, G. M., Kriz, G. S. & Vyvyan, J. R., *Introduction to Spectroscopy* (5th ed.), Cengage Learning, 2014.
- [14] J. Coates, *Interpretation of Infrared Spectra, a Practical Approach.*, John Wiley & Sons, 2000.

- [15] Simon, P., & Gogotsi, Y., "Materials for Electrochemical Capacitors," *Nature Materials*, 7, pp. 845-854, 2008.
- [16] Sevilla, M., & Mokaya, R., "Energy storage Applications of Activated Carbons: Super capacitors and Hydrogen Storage," *Energy and Environmental Science*, 7(4), pp. 1250-1280, 2014.
- [17] Ferrari, A. C., & Robertson, J., "Interpretation of Raman Spectra of Disordered and Amorphous Carbon," *Physical Review B*, 61(20), p. 14095–14107, 2000.
- [18] Zhou, Y., Bao, Q., Tang, L. A. L., Zhong, Y. & Loh, K. P., "Hydrothermal Dehydration for the "Green" Reduction of Exfoliated Graphene Oxide to Graphene and Demonstration of Tunable Optical Limiting Properties," *Advanced Materials*, 21(23), pp. 2363-2368, 2014.
- [19] Zhang, J., Zhao, X. & Tian, Y., "Nitrogen Doping and Reduction of Graphene Oxide via Chicken Feather Keratin Hydrolysate," *Journal of Materials Chemistry*, 20(32), p. 6755–6761, 2010.
- [20] Luo, J., Jang, H. D. & Huang, J., "Effect of Sheet Morphology on the Scalability of Graphene-based Ultracapacitors," *American Chemical Society Nano*, 7(2), pp. 1464-1471, 2013.