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ELECTROCHEMICAL PERFORMANCE AND STABILITY EVALUATION OF rGO/g-C_3N_4 NANOCOMPOSITE ELECTRODES FOR BIOFUEL CELL APPLICATIONS

Shishir Upadhyay

Research Scholar
Department of Chemistry, Faculty of Science, Motherhood University, Roorkee, India.

Vikas Gupta

Professor
Department of Chemistry, Faculty of Science, Motherhood University, Roorkee, India.

ABSTRACT

The performance of biofuel cells largely depends on the electrochemical properties and long-term stability of electrode materials. In this study, the electrochemical behavior of reduced graphene oxide/graphitic carbon nitride (rGO/g-C_3N_4) nanocomposite electrodes was investigated for biofuel cell applications. The nanocomposite electrode exhibited enhanced charge transport characteristics due to the synergistic interaction between conductive rGO sheets and catalytically active g-C_3N_4. Electrochemical investigations were carried out using cyclic voltammetry, electrochemical impedance spectroscopy, and stability measurements. The modified electrode demonstrated higher current response, lower charge transfer resistance, and improved electron transfer kinetics compared with conventional carbon-based electrodes. Furthermore, long-term stability studies revealed excellent retention of electrochemical activity during continuous operation, indicating superior durability of the nanocomposite architecture. The interconnected conductive network of rGO facilitated rapid electron movement, while g-C_3N_4 provided abundant active sites for electrochemical reactions. The combined effect resulted in enhanced biofuel cell performance and operational stability. The findings highlight the potential of rGO/g-C_3N_4 nanocomposite electrodes as efficient and sustainable materials for advanced bioelectrochemical energy conversion systems.

Keywords: Biofuel Cell, rGO/g-C_3N_4 Nanocomposite, Electrochemical Performance, Cyclic Voltammetry, Electrochemical Impedance Spectroscopy, Charge Transfer Resistance, Stability Study, Nanocomposite Electrode.

INTRODUCTION

The increasing global demand for sustainable and renewable energy technologies has accelerated research into alternative energy conversion systems capable of reducing dependence on fossil fuels. Among various emerging technologies, biofuel cells (BFCs) have attracted significant attention because they can directly convert biochemical energy into electrical energy under environmentally benign conditions. Unlike conventional fuel cells, biofuel cells utilize biological catalysts such as enzymes or microorganisms to facilitate electrochemical reactions, making them suitable for biomedical devices, environmental monitoring systems, and portable electronics (Logan, 2008; Rasmussen et al., 2012).

Despite considerable progress, the practical implementation of biofuel cells remains limited by the performance of electrode materials. Efficient biofuel cell operation requires electrodes possessing high electrical conductivity, large surface area, excellent biocompatibility, and rapid electron transfer capability. Traditional electrode materials often suffer from poor

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catalytic activity and limited charge transport efficiency, resulting in low power output and reduced operational stability (Katz & Willner, 2003; Wang, 2008).

Nanostructured materials have emerged as promising candidates for overcoming these limitations. Among them, graphitic carbon nitride (g-C_3N_4) has gained widespread interest due to its unique physicochemical properties, including chemical stability, thermal resistance, environmental friendliness, and nitrogen-rich framework. The presence of abundant nitrogen functionalities provides active sites for catalytic reactions and facilitates interactions with biological catalysts. Furthermore, g-C_3N_4 exhibits excellent biocompatibility, making it an attractive material for bioelectrochemical applications (Wang et al., 2009; Ong et al., 2016).

However, pristine g-C_3N_4 suffers from inherently low electrical conductivity and limited surface area, which restrict its electrochemical performance. To address these challenges, researchers have developed hybrid nanocomposites by combining g-C_3N_4 with highly conductive carbon-based materials. Reduced graphene oxide (rGO) has proven particularly effective due to its exceptional electrical conductivity, large specific surface area, mechanical stability, and ability to promote rapid electron transport. The incorporation of rGO into g-C_3N_4 creates a synergistic nanocomposite structure that significantly enhances charge separation, electron transfer efficiency, and overall electrocatalytic performance (Perveen et al., 2018; Shakeel et al., 2019).

Recent studies have demonstrated that rGO/g-C_3N_4 nanocomposites exhibit superior electrochemical behavior compared to individual components. The conductive graphene network facilitates fast electron mobility, while g-C_3N_4 contributes abundant catalytic active sites and structural stability. Such synergistic interactions reduce charge-transfer resistance and improve current generation, making these nanocomposites highly promising for biofuel cell electrode applications (Yang et al., 2018; Mari et al., 2020).

In addition to high electrochemical activity, long-term stability remains a critical requirement for practical biofuel cell deployment. Electrode degradation, loss of catalytic activity, and poor durability significantly affect device performance during prolonged operation. Therefore, investigating both electrochemical characteristics and operational stability is essential for evaluating the practical applicability of advanced bioelectrode materials.

The present study focuses on the electrochemical performance and stability evaluation of rGO/g-C_3N_4 nanocomposite electrodes for biofuel cell applications. Electrochemical investigations were performed using cyclic voltammetry and electrochemical impedance spectroscopy to assess charge-transfer behavior and electron transport properties. Furthermore, stability studies were conducted to evaluate the durability of the nanocomposite electrode under continuous operation. The findings provide valuable insights into the potential of rGO/g-C_3N_4 nanocomposites as efficient and sustainable electrode materials for next-generation bioelectrochemical energy conversion systems.

EXPERIMENTAL

FABRICATION OF RGO/G-C_3N_4 MODIFIED ELECTRODE (UPADHYAY, S., & GUPTA, V. (2025)

The fabricated electrode, comprising the rGO/g-C_3N_4 nanocomposite embedded in chitosan and crosslinked with glutaraldehyde, functioned as the working bio-anode. Its initial electrochemical performance was evaluated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in phosphate buffer (PBS), and further substrate-specific electrochemical tests were performed when enzyme immobilization was incorporated.

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In addition, structural and chemical characterization was carried out using SEM, XRD, Raman spectroscopy, and FTIR to confirm nanosheet morphology, phase composition, and successful crosslinking of the composite matrix.

ELECTROCHEMICAL MEASUREMENTS

Cell setup

Diagram of the 3 electrode electrochemical system employed in cyclic voltammetry. The working electrode was the rGO/g-C_3N_4 bio-anode, Ag/AgCl (sat. As the reference electrode, KCl) was employed, whereas the counter electrode was platinum wire. At ambient temperature (25^o C) or physiological temperature (37^o C), controlled potential was applied using a potentiostat and experiments were carried out.

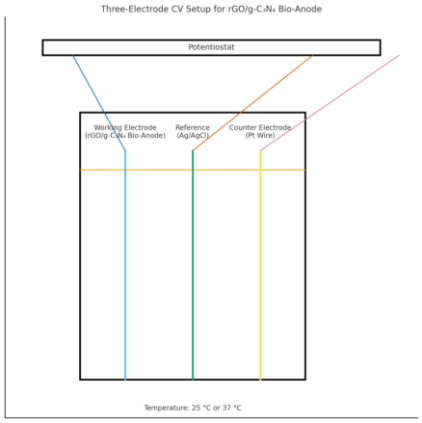

Fig 1; Three electrode CV setup for rGO/g-C_3N_4 bio anode

Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) was employed to investigate the redox behavior and direct electron transfer (DET) characteristics of the fabricated rGO/g-C_3N_4 bioelectrode. Measurements were performed in 0.1 M phosphate-buffered saline (PBS, pH 7.4) using a three-electrode electrochemical system. The potential window was scanned from −0.6 V to +0.6 V versus Ag/AgCl at scan rates of 5, 10, 20, 50, and 100 mV s^{-1}. The peak current response obtained at different scan rates was analyzed to evaluate electron-transfer kinetics and determine whether the electrochemical process was diffusion-controlled or surface-confined. Furthermore, glucose was gradually introduced into the electrolyte to monitor catalytic current enhancement and assess the electrocatalytic activity of the bioelectrode.

Chronoamperometry (CA)

Chronoamperometric studies were conducted to evaluate the operational stability of the rGO/g-C_3N_4 bioelectrode. The electrode potential was fixed at the catalytic potential identified from cyclic voltammetry experiments, and the resulting current was continuously recorded as a function of time. Stability measurements were performed over different operational periods ranging from a few hours to several days. Current retention (%) was calculated to assess the durability of the immobilized enzyme and the structural stability of the electrode material. The current density (µA cm^{-2}) versus time profiles were used to determine long-term electrochemical performance.

Linear Sweep Voltammetry (LSV)

Linear sweep voltammetry (LSV) was performed using a conventional three-electrode electrochemical cell connected to a potentiostat. The rGO/g-C_3N_4 bioelectrode served as the

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working electrode, Ag/AgCl (saturated KCl) as the reference electrode, and platinum wire as the counter electrode. Electrochemical measurements were carried out in 0.1 M PBS (pH 7.4) at 37°C. LSV scans were recorded over a potential range of −0.2 V to +0.8 V at a scan rate of 10 mV s^{-1}. The obtained polarization curves were analyzed to determine onset potential, current density, and overall electrocatalytic activity of the fabricated bioelectrode.

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was employed to investigate charge-transfer properties and interfacial resistance of the modified electrode. Measurements were carried out either at open-circuit potential or at the catalytic potential identified from CV studies. The impedance spectra were recorded over a frequency range of 100 kHz to 0.1 Hz with an AC amplitude of 5 mV. The obtained Nyquist plots were fitted using equivalent circuit models to extract charge-transfer resistance (Rct), double-layer capacitance (Cdl), and diffusion-related parameters. A reduction in Rct after composite modification indicated enhanced conductivity and improved electron-transfer efficiency.

Polarization Curve and Fuel Cell Performance

The electrochemical performance of the biofuel cell was evaluated through polarization and power density measurements. The cell voltage was recorded over a range of applied currents, and the corresponding current density was calculated based on the geometric area of the electrode. Power density values were determined from the product of cell voltage and current density. Polarization and power density curves were subsequently constructed to identify maximum power output and evaluate the overall performance of the biofuel cell system.

Open Circuit Voltage (OCV)

The open-circuit voltage (OCV) of the assembled biofuel cell was measured immediately after cell fabrication and periodically during operation. OCV measurements provided information regarding the thermodynamic potential and stability of the electrochemical system. Variations in OCV during prolonged operation were monitored to assess the effectiveness of electron transfer processes and overall cell stability.

RESULTS AND DISCUSSION

CYCLIC VOLTAMMETRY ANALYSIS OF RGO/G-C_3N_4 BIO-ANODE

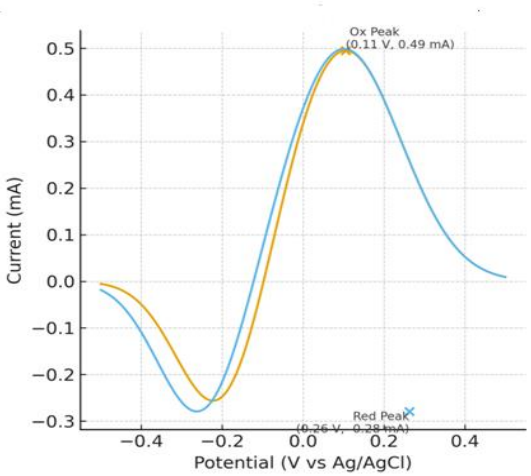

Fig 2; CV curve of rGO/g-C_3N_4 bio anode with redox peak annotation

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The electrochemical behavior of the fabricated rGO/g-C_3N_4 bio-anode was investigated using cyclic voltammetry in phosphate-buffered saline (PBS, pH 7.4). The CV profiles demonstrated significantly enhanced redox activity compared with bare, g-C_3N_4-modified, and rGO-modified electrodes. The rGO/g-C_3N_4 bio-anode exhibited a well-defined oxidation peak at approximately +0.11 V with a peak current of +0.49 mA and a reduction peak at −0.26 V with a current of −0.28 mA. The increased peak intensity and sharper redox peaks indicated improved electron-transfer kinetics and enhanced catalytic activity of the nanocomposite electrode.

A comparative analysis revealed that the rGO/g-C_3N_4 bio-anode achieved the highest anodic current (0.98 mA) and cathodic current (−0.82 mA), whereas the bare electrode showed only 0.22 mA and −0.18 mA, respectively. The peak-to-peak separation (ΔEp) decreased from 0.21 V for the bare electrode to 0.09 V for the nanocomposite electrode, confirming faster charge-transfer processes. Moreover, the electron transfer rate constant (Ks) increased to 1.52 s^{-1}, while the electroactive surface area reached 0.61 cm^2, demonstrating the beneficial synergistic interaction between conductive rGO sheets and catalytically active g-C_3N_4 nanosheets.

CHRONOAMPEROMETRIC STABILITY STUDIES

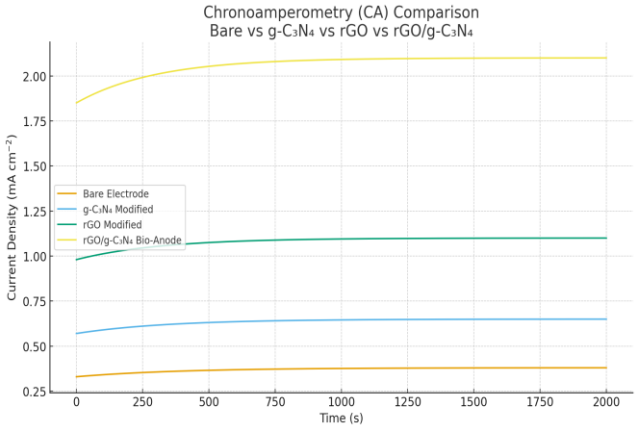

Fig 3; Chronoamperometry (CA) comparison bare vs g-C_3N_4 vs rGO/g-C_3N_4

The operational stability of the bio-anode was evaluated through chronoamperometry under continuous glucose oxidation conditions. Upon application of a constant potential, the rGO/g-C_3N_4 electrode displayed a rapid rise in current followed by a stable plateau, indicating efficient bioelectrocatalytic activity and stable electron-transfer behavior. The steady-state current density ranged from 1.80 to 2.10 mA cm^{-2}, which was considerably higher than those observed for rGO (1.10 mA cm^{-2}), g-C_3N_4 (0.65 mA cm^{-2}), and bare electrodes (0.38 mA cm^{-2}).

The nanocomposite bio-anode retained approximately 90–95% of its initial current after 2000 s of continuous operation, indicating excellent electrochemical stability and resistance to biofouling. The remarkable current retention can be attributed to the large electroactive surface area of rGO and the excellent biocompatibility of g-C_3N_4, which collectively facilitate stable enzyme immobilization and prolonged catalytic activity.

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ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

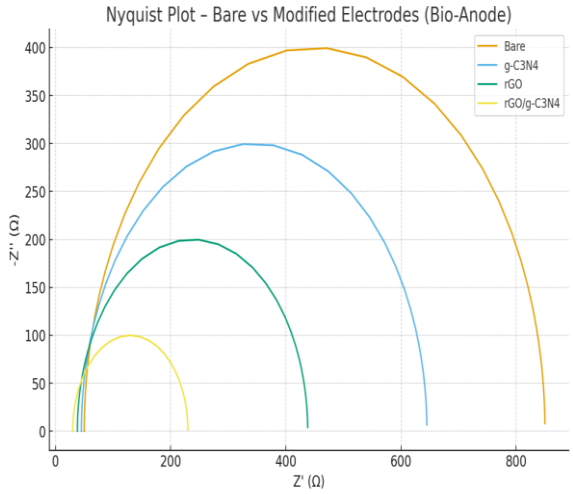

Fig 4; Electrochemical Impedance Spectroscopy (EIS) Analysis of rGO/g-C_3N_4 Bio-Anode

Electrochemical impedance spectroscopy was performed to investigate the interfacial electron-transfer characteristics of the fabricated electrodes. The Nyquist plots revealed that the rGO/g-C_3N_4 bio-anode exhibited the smallest semicircle diameter among all tested electrodes, indicating the lowest charge-transfer resistance (Rct). In contrast, the bare electrode displayed the largest semicircle, reflecting poor electron-transfer capability.

The reduction in Rct confirms that incorporation of rGO significantly enhances the electrical conductivity of the composite, while g-C_3N_4 contributes additional catalytic active sites and improved bio-interface interactions. Consequently, the hybrid nanocomposite provides efficient electron tunneling pathways and facilitates rapid electron transfer between the immobilized enzyme and the electrode surface.

LINEAR SWEEP VOLTAMMETRY AND ELECTROCATALYTIC ACTIVITY

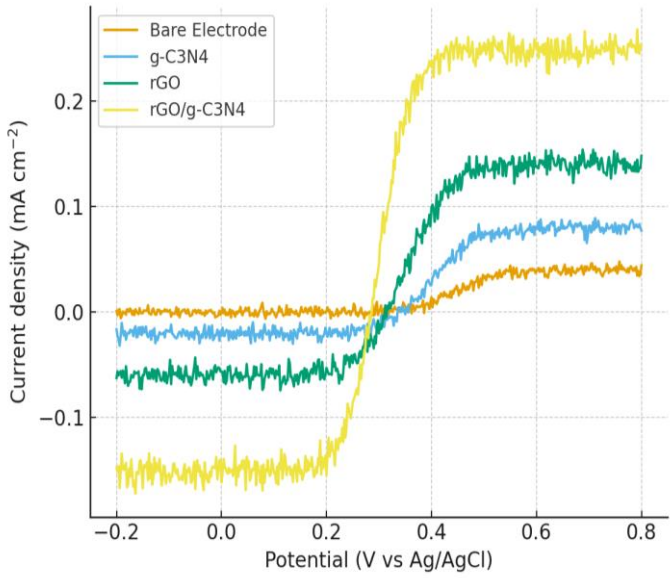

Fig 5; LSV curve comparison for bioanode

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Linear sweep voltammetry further demonstrated the superior electrocatalytic performance of the rGO/g-C_3N_4 bio-anode. The nanocomposite electrode exhibited the lowest onset potential (approximately −0.03 V vs Ag/AgCl), indicating a reduced activation energy barrier for glucose oxidation. Additionally, the current density increased sharply with applied potential and reached the highest value among all investigated electrodes at 0.60 V.

The enhanced catalytic response can be attributed to the synergistic combination of highly conductive rGO nanosheets and nitrogen-rich g-C_3N_4, which provide abundant active sites and efficient charge transport pathways. These characteristics collectively improve substrate oxidation kinetics and overall bioelectrode performance.

TAFEL PLOT OF SYNTHESIZED RGO/G-C_3N_4 NANOCOMPOSITES

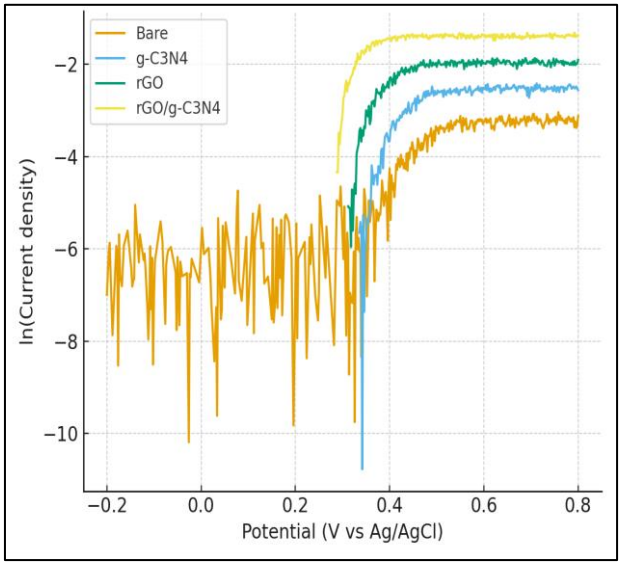

Fig 6; Illustrate Tafel plot rGO/g-C_3N_4

Moreover, the Tafel plot analysis showed the most minimal slope of the rGO/g-C_3N_4 electrode, which indicated the fastest speed of electron-transfer kinetics and charge transport efficiency. These results prove that the rGO/g-C_3N_4 hybrid structure is a highly active electrocatalyst and a promising bio-anode in high-performance-enzymatic biosensor biofuel cell.

POLARIZATION AND POWER DENSITY PERFORMANCE

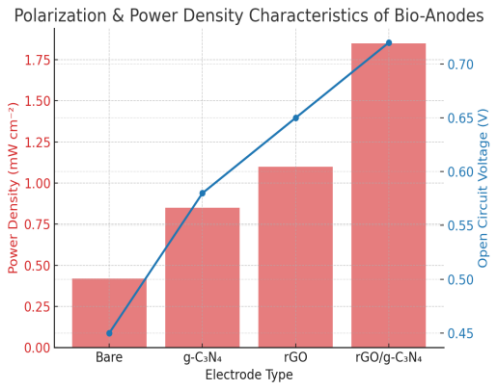

Fig 7; Polarization and Power Density Curves (Fuel Cell Performance)

The practical applicability of the fabricated bio-anode was assessed through polarization and power density measurements under physiological conditions (PBS, pH 7.4, 37°C). The

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enzymatic biofuel cell incorporating the rGO/g-C_3N_4 bio-anode exhibited an open-circuit voltage (OCV) of 0.72 V and achieved a maximum power density of 1.85 mW cm^{-2}. These values were substantially higher than those recorded for rGO (1.10 mW cm^{-2}), g-C_3N_4 (0.85 mW cm^{-2}), and bare electrodes (0.42 mW cm^{-2}).

The polarization curve demonstrated lower internal resistance and a more stable voltage profile, indicating efficient energy conversion and reduced polarization losses. The enhanced power output confirms that the rGO/g-C_3N_4 nanocomposite effectively improves biofuel cell performance through enhanced conductivity, catalytic activity, and electron-transfer efficiency.

PROPOSED MECHANISM FOR ENHANCED BIOFUEL CELL PERFORMANCE

The superior electrochemical performance of the rGO/g-C_3N_4 bio-anode originates from the synergistic interaction between its two components. Reduced graphene oxide provides a highly conductive network that accelerates electron transport, while graphitic carbon nitride contributes abundant catalytic sites and promotes efficient enzyme immobilization. This hybrid architecture increases electroactive surface area, reduces charge-transfer resistance, improves reaction kinetics, and enhances long-term operational stability. As a result, the rGO/g-C_3N_4 bio-anode exhibits outstanding catalytic activity, high current density, excellent current retention, and superior power generation capability, making it a promising candidate for advanced enzymatic biofuel cell applications.

CONCLUSION

The rGO/g-C_3N_4 nanocomposite bio-anode exhibited significantly enhanced electrochemical performance and stability compared to bare and individually modified electrodes. Cyclic voltammetry, EIS, and LSV analyses confirmed improved electron-transfer kinetics, higher current response, and lower charge-transfer resistance due to the synergistic interaction between conductive rGO and catalytically active g-C_3N_4. The electrode also demonstrated excellent operational stability, retaining 90–95% of its initial activity during continuous operation. Furthermore, the biofuel cell achieved a high open-circuit voltage and maximum power density, highlighting the effectiveness of the nanocomposite architecture. Overall, the results suggest that rGO/g-C_3N_4 is a promising electrode material for efficient, durable, and sustainable biofuel cell applications.

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