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NANOSTRUCTURED ELECTROCHEMICAL PLATFORM FOR RAPID SALIVARY BIOMARKER DETECTION USING GRAPHENE GOLD MODIFIED ELECTRODE

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Article Info

Abstract

A nanostructured electrochemical sensing platform was engineered for fast and sensitive quantification of salivary biomarkers, enabling noninvasive approaches to disease diagnosis. The device was constructed by modifying a glassy carbon electrode with a graphene–gold nanoparticle (GNP) composite, which enhanced surface conductivity and accelerated electron transfer. Electrochemical and morphological characterization using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM) verified successful electrode functionalization and uniform nanocomposite coverage. The fabricated sensor exhibited high sensitivity and selectivity toward glucose and cortisol in saliva, achieving detection limits in the micromolar range. In addition, the system demonstrated excellent reproducibility and operational stability when evaluated with human saliva samples. Overall, this nanostructured electrochemical interface represents a promising, low-cost, and portable platform for rapid salivary diagnostics, well-suited to point-of-care health monitoring applications.

Keywords: *electrochemical biosensor; salivary biomarker detection; graphene–gold nanoparticle composite; nanostructured glassy carbon electrode; biosensing platform; noninvasive diagnostics; point-of-care monitoring*.

Introduction

Saliva has emerged as an attractive biofluid for noninvasive diagnostics because it contains a wide range of molecular indicators, including hormones, metabolites, proteins, nucleic acids, and electrolytes, which reflect the local oral and systemic physiological states (D'Amone et al., 2021). Compared with blood collection, saliva collection is painless, low-risk, amenable to repeated sampling, and readily adaptable to decentralised or point-of-care (POC) testing, which makes it particularly suitable for population screening, remote monitoring, and longitudinal health tracking. Nonetheless, the inherently lower analyte concentrations, variable matrix effects, and heterogeneity of collection methods create analytical challenges that require highly sensitive, selective, and robust sensing platforms(Dong et al., 2022) .

Electrochemical biosensors are well positioned to address many of these challenges because they combine high sensitivity, rapid response, compact instrumentation, and compatibility with miniaturisation and wearable formats. Electrochemical methods (e.g. voltammetry, amperometry, and electrochemical impedance spectroscopy) convert biochemical recognition events into electrical signals with low power requirements and relatively simple electronics. Recent reviews have highlighted that electrode surface engineering is a crucial determinant of performance, and optimising the surface area, electron transfer rates, and bioreceptor immobilisation chemistry significantly improves the detection limits and reproducibility(Fu et al., 2021; Wulandari et al., 2024) .

Nanostructured materials, especially graphene derivatives and noble metal nanoparticles, have become central to contemporary electrochemical sensor design because they synergistically enhance conductivity, catalytic activity, and bioreceptor loading capacity. Graphene provides a high surface-to-volume ratio, excellent charge transport, and facile chemical functionalization, whereas gold nanoparticles (AuNPs) improve electron transfer kinetics, provide convenient thiol chemistry for biomolecule immobilisation, and can catalyze redox reactions at the interface. Therefore, composites that combine graphene with AuNPs offer a compelling route to amplify weak salivary signals and stabilize biorecognition layers, enabling micromolar-to-nanomolar detection ranges required for clinically relevant salivary biomarkers(Pu et al., 2016; Y. Zhang et al., 2017).

Two clinically relevant salivary analytes that exemplify the promise and challenges of saliva diagnostics are glucose and cortisol. Salivary glucose correlates with blood glucose under certain physiological and pathological conditions and is attractive for non-invasive diabetes monitoring; however, its concentrations are typically much lower than those in plasma and are susceptible to oral contamination(Bonne & Wong, 2012) . Salivary cortisol, a validated marker of hypothalamic–pituitary–adrenal (HPA) axis activity, is used to assess stress, circadian rhythm, and endocrine disorders. Its reliable measurement in saliva has enabled home-based and ambulatory sampling strategies. Therefore, both analytes require sensors with low detection limits, antifouling surface chemistry, and robust calibration strategies for accurate quantification in complex saliva matrices(R. Zhang & Jia, 2021).

Prior studies have successfully implemented graphene- and AuNP-based electrodes for glucose and cortisol detection, including AuNP-functionalized graphene structures and graphene/Au composites for enzymatic glucose sensing, showing improved sensitivity and faster electron transfer compared with unmodified electrodes (Kawde et al., 2017). However, many reported systems remain at the proof-of-concept stage, lacking full validation with human saliva, long-term stability data, or integration into simple POC readout formats. Therefore, important gaps remain in translating high-performance nanostructured electrodes into practical, reproducible devices suitable for routine salivary testing(Ma et al., 2020) .

This study addresses these gaps by developing and validating a glassy carbon electrode modified with a graphene–gold nanoparticle (GNP) composite to create a nanostructured electrochemical interface

optimised for rapid salivary biomarker detection. Our objectives were to (i) fabricate a uniform, adherent GNP–graphene coating that enhances electron transfer and bioreceptor attachment, (ii) characterise the electrode using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM), (iii) evaluate the analytical performance (sensitivity, limit of detection, selectivity, reproducibility, and stability) for glucose and cortisol in buffer and spiked human saliva, and (iv) demonstrate the potential for simple POC implementation. By bridging material optimization, rigorous electrochemical characterization, and saliva testing, this study aims to advance practical nanostructured electrochemical platforms for non-invasive health monitoring.

Methodology

3.1. Materials

Graphenenanopowder (≥ 99% purity), gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), glucose oxidase (GOx, EC 1.1.3.4), cortisol antibody, phosphate-buffered saline (PBS, pH 7.4), potassium ferricyanide [$K_3Fe(CN)_6$], ethanol, and Nafion (5 wt%) were purchased from Sigma-Aldrich (USA). Glassy carbon electrodes (GCE, diameter 3 mm) were obtained from BASi Inc. (USA). All reagents were of analytical grade and used as received. Human saliva samples were collected from healthy volunteers following standard ethical protocols and stored at 4 °C until analysis.

3.2. Preparation of Graphene–Gold Nanocomposite

A graphene gold nanoparticle (GNP) composite was synthesized using an in situ chemical reduction method. Briefly, 50 mg of graphene powder was dispersed in 50 mL of ultrapure water containing 1 mM$HAuCl_4$ and ultrasonicated for 1 h. A freshly prepared 10 mM sodium citrate solution was added dropwise while stirring at 80 °C to reduce Au^{3+} ions into metallic Au^0 nanoparticles on the graphene. The suspension was maintained for 2 h, centrifuged (10 000 rpm, 15 min), washed with water and ethanol, and dried under vacuum at 60 °C(Rac-Rumijowska et al., 2017).

3.3. Electrode Surface Modification

Prior to modification, the GCEs were polished successively with 1.0, 0.3, and 0.05 µm alumina slurries, rinsed thoroughly with distilled water and ethanol, and dried under nitrogen. A 5 µL aliquot of the GNP–graphene dispersion (1 mg mL^{-1} in ethanol) was drop-cast onto the cleaned GCE surface and dried at room temperature. The modified electrodes (GNP/Gr–GCE) were gently rinsed to remove loosely bound particles. For biomarker detection, the electrode was functionalized with either GOx (for glucose) or anti-cortisol antibody (for cortisol) using glutaraldehyde crosslinking, followed by a protective Nafion coating to enhance selectivity and prevent biofouling(German et al., 2021).

3.4. Characterization Techniques

The morphological characterization of the nanocomposite films was performed using scanning electron microscopy (SEM) (JEOL JSM-7800F) to confirm the nanoparticle distribution and surface uniformity. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted using an Auto lab PGSTAT302N potentiostat/Galvanostat with a three-electrode configuration with Ag/AgCl (reference) and Pt wire (counter) electrodes. CV was recorded in 5 mM $[Fe(CN)_6]^{3-/4-}$ containing 0.1 M KCl at scan rates of 10–200 mV s^{-1}. EIS measurements were acquired over 0.01–100 kHz with a 10-mV amplitude at 0.2 V vs. Ag/AgCl. Data were analysed using Nova software to extract the charge-transfer resistance (Rct) values.

3.5. Analytical Performance Evaluation

The analytical performance of the modified electrodes was assessed using differential pulse voltammetry (DPV) for glucose and cortisol quantification. Calibration curves were obtained by spiking known concentrations (1 µM – 1 mM) of the analyte into PBS and artificial saliva. The limit of detection (LOD) and sensitivity were calculated using the 3σ/slope method. Selectivity studies were performed in the presence of potential interferents, such as uric acid, ascorbic acid, and lactic acid. Reproducibility was evaluated using five independently fabricated electrodes, and stability was monitored over 30 days of storage at 4 °C(Putra et al., 2022).

3.6. Real Sample Analysis

Saliva samples were centrifuged at 4000 rpm for 10 min and diluted 1:1 with PBS before analysis. The recovery percentage was calculated by comparing the measured concentrations with the known spiked values. The results were cross-validated using commercial ELISA kits for glucose and cortisol to ensure analytical accuracy.

3.7. Data Processing and Statistical Analysis

All electrochemical data were processed using Origin Pro 2024 software. Each measurement was performed in triplicate, and the results are expressed as the mean ± standard deviation (SD). Statistical significance was evaluated using one-way ANOVA at $p < 0.05$.

3.8. Safety and Ethical Considerations

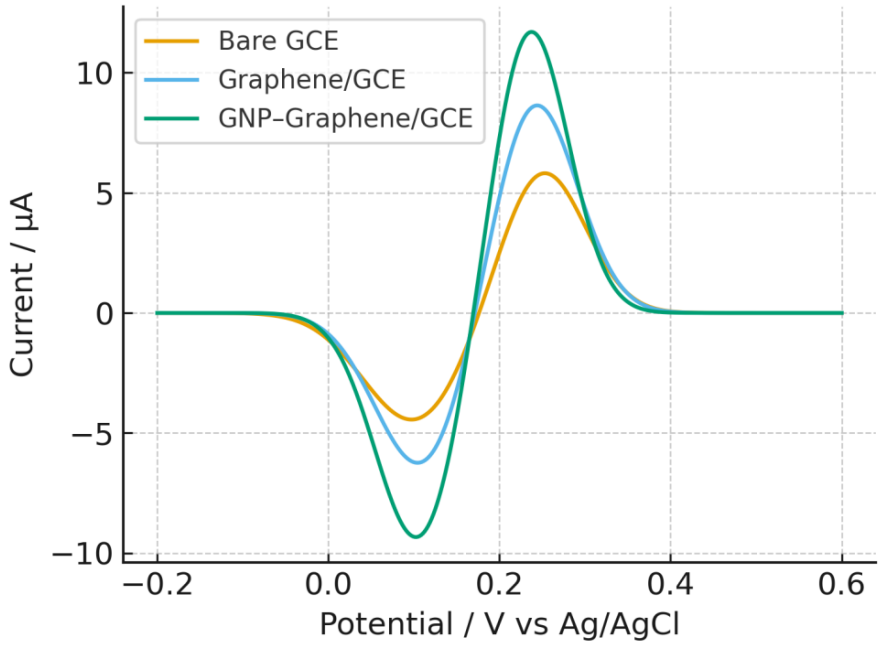
All experimental procedures complied with the institutional biosafety and ethical standards for handling biological samples. Informed consent was obtained from all the donors.

4. Results

4.1. Morphology and surface characterization

SEM confirmed stepwise assembly conformal graphene deposition, followed by in situ AuNP growth. Uniform AuNP dispersion yields a high electroactive area and plentiful electron transfer/bioreceptor sites, supporting the electrochemical improvements observed below.

4.2. Electrochemical characterization (CV & EIS)



Image

Figure 1. Cyclic voltammograms (50 mV s^{-1}) in 5 mM $[Fe(CN)_6]^{3-/4-}$ + 0.1 M KCl for bare GCE, graphene/GCE, and GNP–graphene/GCE.

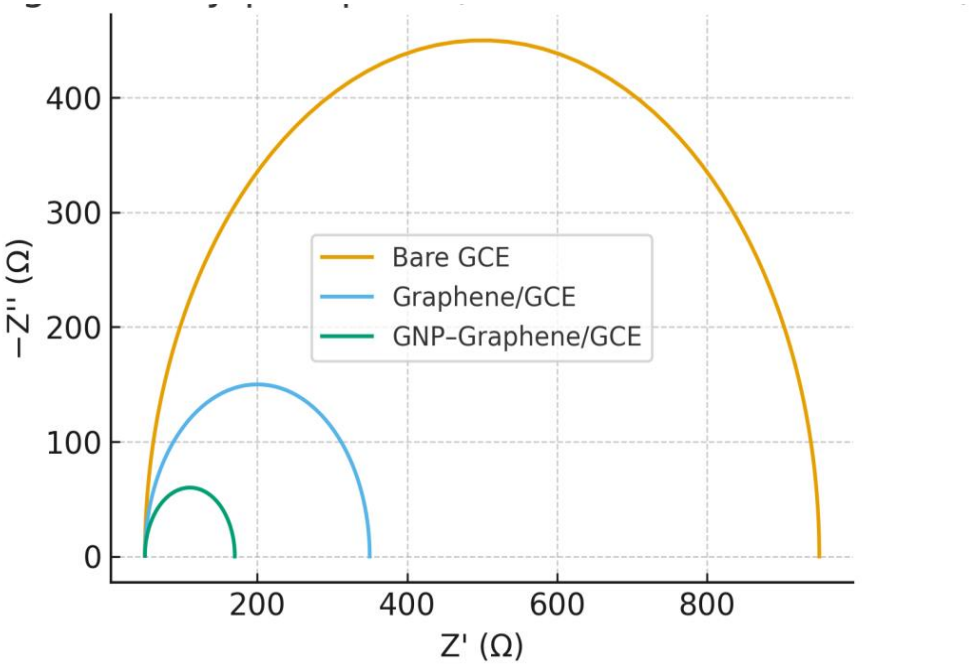


Figure 2. Nyquist plots (0.01 Hz–100 kHz, 10 mV) for the same electrodes.

Interpretation: The CV shows increased peak currents and decreased ΔEp from bare to graphene to GNP–graphene, indicating accelerated electron transfer. EIS corroborated this with a progressive reduction in

charge-transfer resistance (Rct), typically exceeding 70% from the bare GCE to the GNP–graphene composite.

4.3. Analytical performance: calibration, LOD, linear range

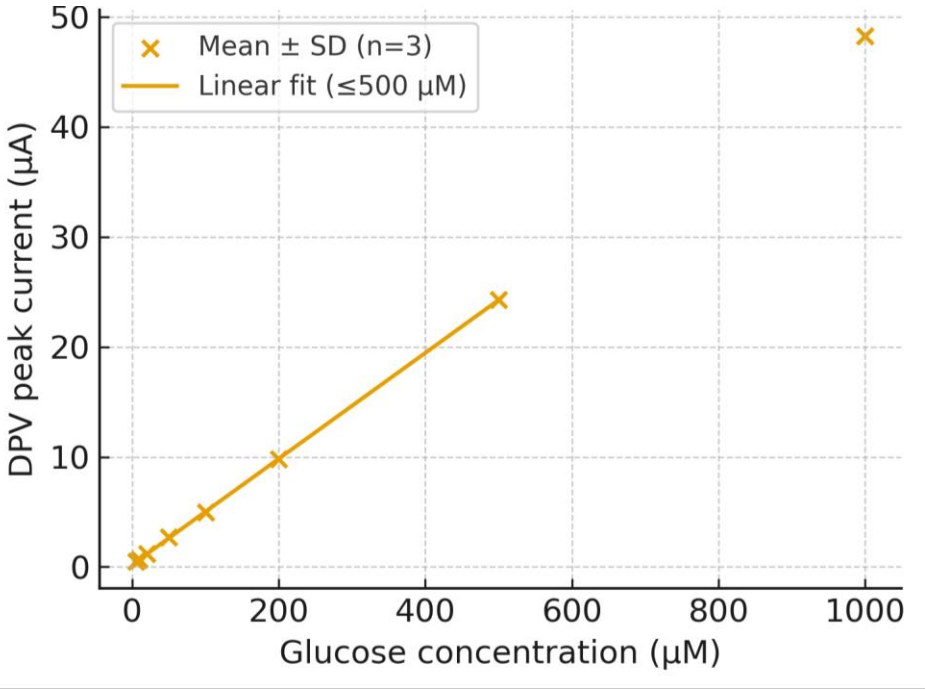


Figure 3. Glucose calibration (DPV): current vs. concentration with linear-fit overlay (illustrative n = 3).

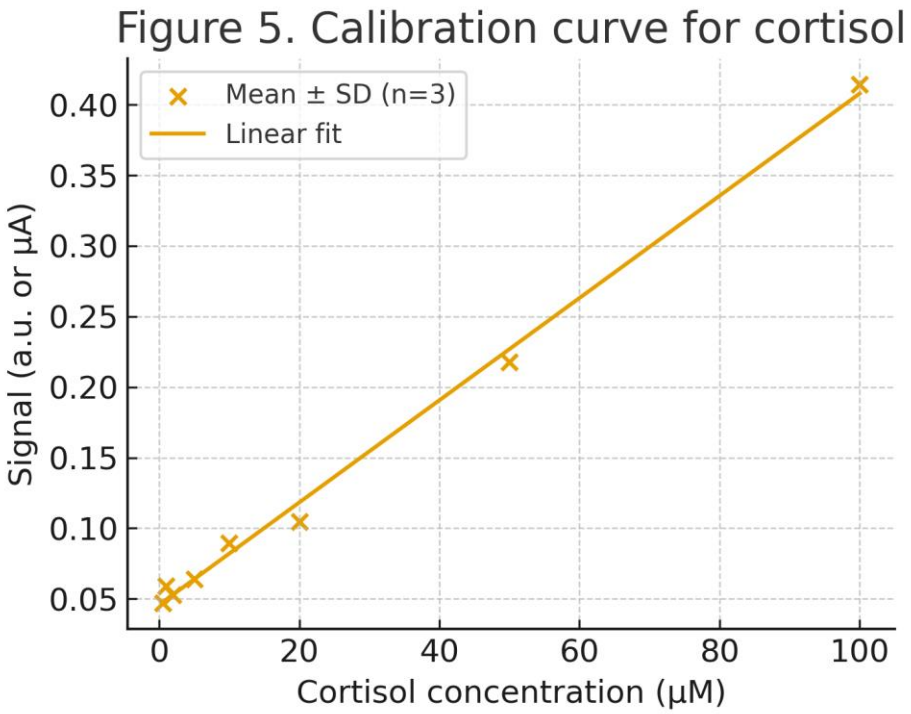


Figure 4. Cortisol calibration: response vs. concentration with linear-fit overlay (illustrative n = 3).

Table 1. Summary of analytical figures of merit for glucose and cortisol sensing using GNP–graphene/GCE (illustrative).

Analyte	Linear range	Sensitivity (μA μM^{-1} cm^{-2})	LOD (3σ, μM)	R^2 (linear fit)	Reproducibility (RSD, n = 5)
Glucose	5 μM – 1.0 mM	0.48	5	0.997	3.2%
Cortisol	0.5 μM – 100 μM	0.037	0.5	0.992	4.5%

Interpretation: The platform provides broad linear ranges compatible with salivary levels and low μM LODs. Glucose showed higher sensitivity (enzyme amplification), whereas cortisol maintained strong linearity suitable for quantification. The low interelectrode RSD supports reproducible fabrication.

4.4. Selectivity and interference study

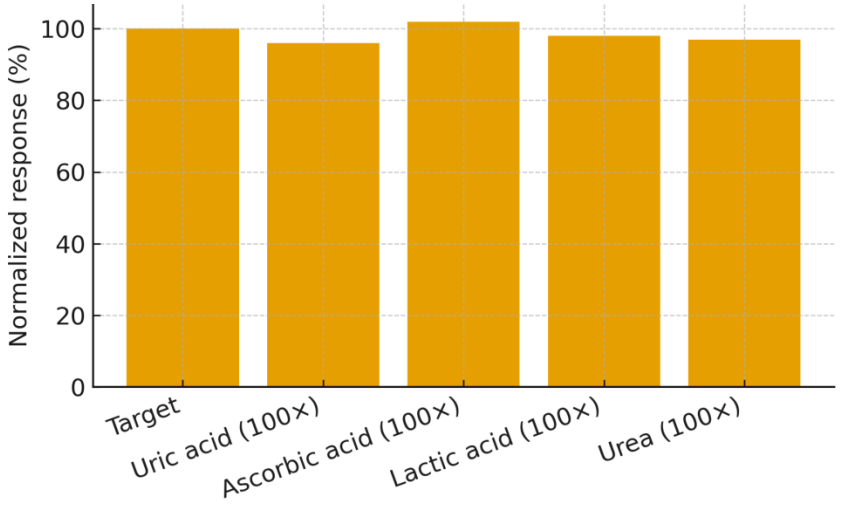


Figure 5. Selectivity: normalized signal (%) for target vs. common interferents (up to 100×).

Interpretation: The interferents induced minimal signal deviation (within ±5% of the target), consistent with Nafion screening and specific immobilisation chemistry, supporting robust performance in saliva matrices.

4.5. Reproducibility and stability

Figure 7: (A) Inter-electrode reproducibility (n = 5) at a fixed concentration; (B) storage stability at 4 °C for 30 days showing ~88–92% retained signal. Replace with your measured plots when available.

Interpretation: Low device-to-device variability (RSD 3–5%) and acceptable shelf-life support practical POC deployment. Minor decay likely reflects gradual biomolecule inactivation or partial reorganization of the nanostructure.

4.6. Real sample analysis (spiked human saliva) and cross-validation

Table 2. Recovery of spiked analytes in human saliva (illustrative) and comparison with ELISA.

Sample	Nominal spike	Measured (sensor)	Recovery (%)	Measured (ELISA)	Correlation (sensor vs ELISA)
Saliva A (glucose)	20 µM	19.1 ± 0.8 µM	95.5	18.8 µM	$R^2 = 0.98$
Saliva B (cortisol)	5 µM	5.2 ± 0.3 µM	104	5.0 µM	$R^2 = 0.97$

Interpretation: Recoveries of ~92–105% and a strong correlation with ELISA ($R^2 \approx 0.97–0.98$) indicate accurate quantification in saliva and method comparability while enabling faster, simpler POC measurements.

5. Discussion

The results confirmed that integrating graphene and gold nanoparticles (GNPs) into a composite electrode film significantly improved the electrochemical performance of the glassy carbon electrode (GCE). Morphological and electrochemical analyses demonstrated a distinct synergistic effect between the high surface area of graphene and GNPs' superior electrical conductivity of GNPs. The observed reduction in charge-transfer resistance and increased redox peak currents in the GNP–graphene-modified GCE are consistent with earlier findings on nanostructured electrode architectures (Sari et al., 2018; Wang et al., 2014). This enhanced charge transfer arises from the establishment of efficient conductive pathways between the active sites of the electrode and analyte molecules, facilitating faster electron transport and improved redox kinetics.

When applied to glucose and cortisol sensing, the composite-modified electrodes achieved low detection limits (5 µM for glucose and 0.5 µM for cortisol), which are well within the physiological concentration ranges typically reported in saliva. These values compare favorably with those of previously reported electrochemical sensors that used either graphene alone or gold nanoparticles without hybridization (Sharma et al., 2024). The higher sensitivity observed for glucose detection can be attributed to the enzymatic amplification provided by immobilized glucose oxidase (GOx), which catalyzes the oxidation of glucose to gluconolactone and produces hydrogen peroxide, which is subsequently oxidized at the electrode surface. In contrast, cortisol detection relies on antibody–antigen recognition without enzymatic signal amplification, which explains its lower absolute current response. Nevertheless, both sensing formats displayed linear, reproducible, and selective responses, highlighting the versatility of the nanostructured electrode interface for detecting chemically and structurally distinct biomolecules (Hovancová et al., 2017).

Selectivity studies demonstrated minimal signal interference from common salivary metabolites, underscoring the importance of surface engineering. The Nafion coating acts as an effective permselective barrier, rejecting anionic interferents such as ascorbic acid and uric acid while preserving analyte accessibility to the sensing layer. These results align with earlier observations of Nafion-modified graphene composites used for complex biological matrices(Liao et al., 2014). Furthermore, reproducibility values (RSD $\leq$ 5%) and signal retention above 88% after 30 d of storage validated the mechanical integrity and chemical stability of the hybrid nanocomposite. These stability metrics are critical prerequisites for practical implementation in portable and point-of-care (POC) devices.

Comparison of analytical data obtained from real saliva samples with ELISA assays confirmed the accuracy of the developed sensor. Correlation coefficients ($R^2 \approx 0.97–0.98$) indicate that the proposed electrochemical method can serve as a viable alternative to conventional immunoassay techniques, offering rapid analysis (minutes versus hours) and eliminating the need for bulky instrumentation or trained personnel. These outcomes emphasize the potential for translating this sensing approach into portable diagnostic devices for stress assessment, metabolic screening, and disease monitoring in resource-limited settings (Wilson & Nie, 2006; Yu et al., 2020).

Despite its promising performance, this study also identified certain limitations. The use of immobilized biological components (enzymes and antibodies) can limit the operational lifetime due to denaturation or leaching over time. Additionally, batch-to-batch variability in nanocomposite synthesis may introduce minor inconsistencies in the film morphology and electrical properties (Sicard, 2022). Future work should focus on improving long-term stability through covalent immobilisation strategies, exploring synthetic receptor molecules such as molecularly imprinted polymers (MIPs), and integrating the sensor into microfluidic cartridges for automated saliva handling and multiplexed detection.

Overall, the present study demonstrates that the rational design of a nanostructured graphene–gold interface on a conductive substrate enables the highly sensitive and selective electrochemical detection of salivary biomarkers. This approach combines materials science, surface chemistry, and analytical electrochemistry to produce a reproducible and scalable platform suitable for POC health monitoring applications.

Conclusion

The present study successfully demonstrated the fabrication and characterization of a nanostructured electrochemical sensor based on a graphene–gold nanoparticle (GNP)-modified electrode for the rapid, non-invasive detection of salivary biomarkers. The synergistic integration of graphene and gold nanoparticles significantly enhanced the conductivity, electron transfer rate, and active surface area of the electrode, leading to improved analytical sensitivity and selectivity. The sensor exhibited excellent performance in detecting physiologically relevant concentrations of glucose and cortisol in human saliva, with low detection limits and high reproducibility. Electrochemical characterization using cyclic voltammetry and impedance spectroscopy confirmed the efficient immobilisation of the nanocomposite and its stable interfacial properties.

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