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ASSESSING THE PH DETECTION CAPABILITIES OF POLYANILINE AND COMPOSITE MATERIALS INVOLVING REDUCED GRAPHENE OXIDE FOR SALIVARY BIOSENSING

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ABSTRACT

Monitoring the pH levels in saliva within the oral cavity holds significant importance, serving as a valuable biomarker for prognosis and diagnosis, reflecting not only oral health but also various metabolic conditions. The lack of easily wearable intraoral pH sensors poses a significant challenge. This paper introduces a study involving the synthesis and assessment of conductive polymer polyaniline compounds for pH biosensing, with the aim of potentially developing intraoral biosensors for saliva analysis. Both reduced graphene oxide-polyaniline (rGO-PANI) and polyaniline (PANI) were employed as sensing materials to determine which material exhibited superior performance in pH biosensors. The study comprehensively evaluated these sensors, taking into account their sensitivity, repeatability, response time, stability, and pH range. Electrodeposition was employed to fabricate the sensors for both sensing materials. A comparative analysis of the performance of the two sensing materials was conducted using zero current potentiometry electrochemical analysis for the pH sensors. The analysis revealed that the rGO-PANI-based pH sensor performed better than the PANI-based pH sensor. These findings suggest that the rGO-PANI-based sensor could serve as a dependable tool for detecting pH variations in salivary analytes.

Keywords: pH sensor; rGO-PANI; PANI; electrodeposition; zero current potentiometry.

INTRODUCTION

The National Institute of Dental and Craniofacial Research (NIDCR) has developed a strategic approach to utilize saliva for clinical diagnostics, as it contains various analytes that can be utilized to assess health and disease status [1]. Saliva-based diagnostics offer a non-invasive method to evaluate the condition of individuals, providing information on their overall physiological state and oral as well as systemic health [2].

Salivary biomarkers have proven valuable in disease diagnosis and monitoring, offering early assessment of malignancy risk, disease progression, and therapy response. This non-invasive and cost-effective diagnostic method allows for accessible collection and storage of saliva, reducing patient discomfort and ensuring the safety of healthcare professionals. Salivary diagnostics exhibit accuracy, with specific biomarkers linked to health and disease [3]. The pH value of saliva can impact biological, physiological, and medical conditions, with fluctuations serving as indicators of various processes [4]. Further investigation is required to understand the clinical significance of pH disparities fully. Electrochemical pH sensors, particularly metal oxide ones, are employed for monitoring pH changes and are well-suited for wearable applications in chronic diseases due to their unique properties [5].

Potentiometric sensors, an electrochemical sensor, are used to determine the concentration of a specific component in a solution by measuring the potential difference between two electrodes [6]. In this study, a potentiometric biosensor was used to detect bioanalytes in saliva at low concentrations and assess the pH of the solution.

Researchers have developed a wearable device with integrated sensors that can quickly measure and monitor various levels in the body, including pH, glucose, urea, salinity, and dopamine, allowing for early-stage disease

detection. Similarly, an intra-oral pH sensor has been created to diagnose and track common diseases by monitoring salivary pH through an electrochemical method [6]. Electrochemical biosensors, crucial for biomarker analysis, require biocompatible materials like nanoporous gold, graphene, carbon nanotubes, and mesoporous carbon [7]. However, there is currently a lack of easily accessible intra-oral pH sensors, vital for identifying and treating health conditions. This study aims to develop pH sensors using different sensing materials and evaluate their performance in terms of sensing capabilities.

EXPERIMENTAL

The electrodeposition method was used for carbon electrodes coated with polyaniline membranes based on Thu et al. [8]. Firstly, 0.2869g of graphene oxide pellets were dissolved in distilled water to obtain 1mg ml-1 of graphene oxide solution. An electrode was dipped in the graphene oxide solution. The film was then electrochemically reduced for ten cycles using the cyclic voltammetry technique with potentials varying from 0 V to 1.2 V. After electrodeposition, the reduced graphene oxide modified screen-printed electrode was rinsed with distilled water and air-dried using nitrogen.

After that, 0.5M sulphuric acid solution was prepared by diluting the concentrated acid with distilled water. The 0.5M sulphuric acid was then mixed with 0.1M aniline. The screen-printed electrode was then dipped into the sulphuric acid and aniline solution. The film was then electro-deposited using a cyclic voltammetry technique with potential varying from -2 V to 9 V. After that, the screen-printed electrode was rinsed with distilled water and air-dried using nitrogen. The rGO-PANI modified screen-printed electrode was prepared.

The PANI-based electrode was fabricated using an electrodeposition method similar to the previous section. A 0.5M sulphuric acid solution was prepared by diluting concentrated acid with distilled water and then mixed with 0.1M aniline. The electrode was dipped into the sulphuric acid and aniline solution, and the film was electro-deposited using cyclic voltammetry with a potential range of -2 V to 9 V. After rinsing and air-drying, the PANI-modified electrode was prepared.

The evaluation of the rGO-PANI and PANI-based pH sensors involved designing pH solutions ranging from pH 5 to 9 and dropping them onto the electrodes. The potential was obtained using the zero current potentiometry method, and the assessment was repeated for each pH solution. The sensitivity, pH range, and sensor response time were evaluated by plotting the results into a sensor response graph and analyzing the data.

In order to assess the repeatability of the sensors, the zero current potentiometry technique was employed to measure the pH range from 5 to 8. This measurement was performed three times for each pH sensor. The acquired data was then utilized to determine the standard deviation for each pH value. By analyzing the standard deviation, the repeatability of both rGO-PANI and PANI-based pH sensors was determined.

To evaluate the stability of the sensors, the zero current potentiometry method was applied to the sensors on three separate occasions over a period of three weeks. The obtained results were sub sequently presented in a graphical format to illustrate the stability of the pH sensors throughout the three-week duration.

RESULTS AND DISCUSSION

The rGO-PANI electrode was fabricated by electrodeposition of aniline and sulphuric acid onto the surface of the rGO-modified screen-printed electrode, as shown in Fig.1.

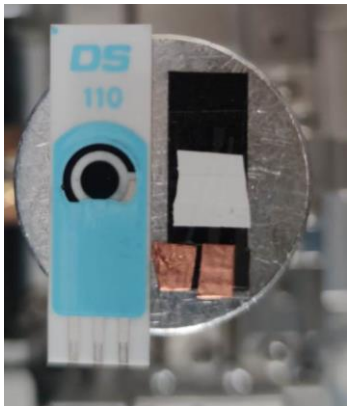

Figure 1. rGO-PANI modified screen-printed and PANI-based fabricated electrodes

The reduction peak of graphene oxide falls considerably in the successive cycles, indicating an irreversible process. The constant increase in current density during the electro-deposition of polyaniline onto rGO suggests PANI spreading throughout the rGO surface, and the transition

between distinct oxidation states of polyaniline can be observed as in Figure 2 (a) and (b).

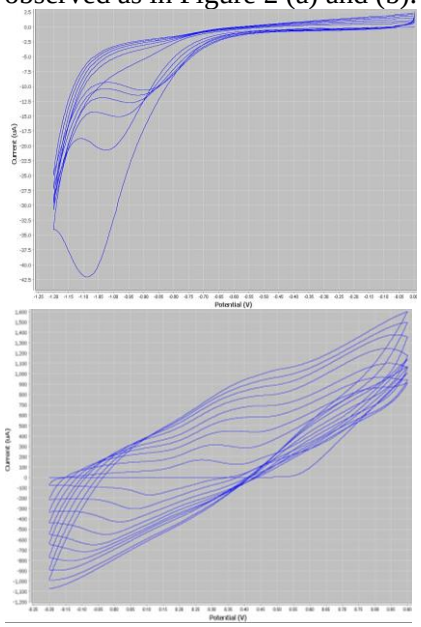

Figure 2. (a) Electro-reduction of graphene oxide coated screen-printed electrode. (b) Electro-deposition of polyaniline onto rGO coated screen-printed electrode.

The PANI electrode was prepared through the electrodeposition of 0.1M aniline and 0.5M sulfuric acid onto the electrode surface. The electrodeposition graph in Figure 3 illustrates the process of polyaniline deposition. The leucoemeraldine form of polyaniline transitions to the emeraldine salt, as indicated by the first anodic wave at +300 mV. The second anodic wave at +750 mV signifies the formation of the completely doped pernigraniline salt. The scan is terminated at 0V to obtain emeraldine.

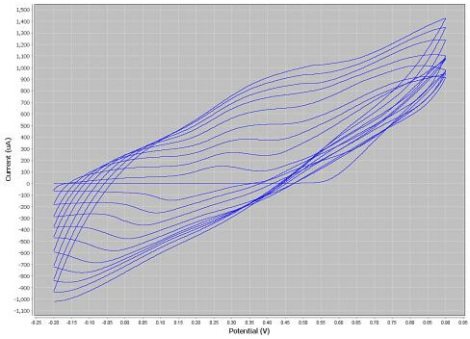

Figure 3. Electro-deposition of polyaniline (PANI) onto electrode.

The sensor response graphs of rGO-PANI and PANI are displayed in Figure 4 and Figure 5, respectively. Based on the sensitivity analysis, rGO-PANI electrode is 78.2 mV/pH, surpassing the ideal Nernstian response value of 59.14 mV/pH. Excluding pH 9.18, the sensitivity obtained is 48.1 mV/pH. The final sensitivity of the rGO-PANI electrode is 48.1 mV/pH for the pH range of pH 5 to pH 8. In addition, the sensitivity of the PANI electrode is 71.4 mV/pH, excluding pH 9.18, the sensitivity obtained is 45 mV/pH. The final sensitivity of the PANI electrode is 45 mV/pH for the pH range of pH 5 to pH 8.

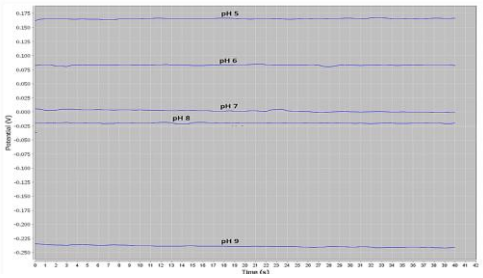

Figure 4. Zero current potentiometry of rGO-PANI.

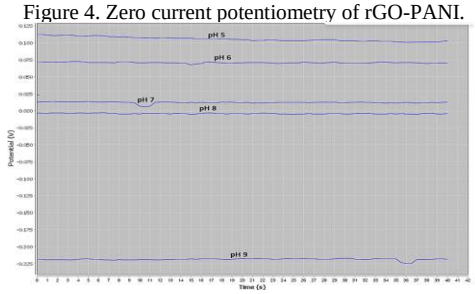

Figure 5. Zero current potentiometry of PANI.

The stability of the rGO-PANI electrode was examined weekly for three weeks. The potential exhibited a slight drift at pH 5, pH 6, and pH 7.64, while pH 8 experienced a slightly higher drift potentially due to contamination during storage. The stability of the PANI electrode is characterised with pH 6 showing a higher drift compared to pH 5, pH 7.64, and pH 8 over the three-week period.

An additional evaluation was conducted after testing the electrode for sensitivity. Solutions of pH 7 and pH 8.5 were prepared to compare the sensor response graph of rGO-PANI and PANI electrode. The outcomes of this study were determined based on several factors including sensitivity, response time, pH range, repeatability, and stability of pH sensors. The use of reduced graphene oxide-polyaniline (rGO-PANI) and polyaniline (PANI) in the sensors was compared. The rGO-PANI sensor showed higher sensitivity compared to the PANI-based sensor. Both sensors had a pH range of 5 to 8, which is suitable for intraoral pH sensing. The response time for both sensors was 1 second, indicating rapid detection of analyte concentration changes. The PANI-based sensor had better repeatability compared to the rGO-PANI-based sensor, with lower standard deviation. The rGO-PANI sensor displayed more stable potential readings

throughout the testing period. The research focused on the fabrication and characterization of electrodes, specifically rGO-PANI and PANI electrodes for salivary pH sensing. The cyclic voltammetry analysis confirmed the reduction of graphene oxide, and the electro-deposition process showed consistent growth of PANI on the rGO surface. The electrode fabrication results laid the foundation for evaluating pH sensing performance. Previous research has also been conducted on rGO-PANI and PANI electrodes, with a focus on their electrical conductivity [9].

CONCLUSION

In summary, the composite material of reduced graphene oxide-polyaniline exhibits the capability to discern alterations in the concentration of analytes, thereby providing insights into the pH levels of said analytes. Consequently, this pH sensor represents a user-friendly tool that may be effectively employed for the purpose of monitoring the salivary pH within the oral cavity, thereby allowing for the assessment of oral well-being and the detection of diverse metabolic states.

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BIOGRAPHY

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