Development of composite conducting polymer with 2D layered and metallic nanosystems for biofunctionalization and electrochemical biosensing applications

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Chapter 7

Conclusions and future direction

This chapter summarizes the key conclusions from the current research, which focuses on the synthesis, characterization, and analysis of the physicochemical and biological properties of PEDOT-PSS and PANI-based nanocomposite electrodes, such as AuNP/GO/PEDOT-PSS, AuNP/WS_2/PEDOT-PSS, and PANI-PVA, for the detection of Glucose and AF-B_1. Additionally, it discusses the future research prospects in this field.

7.1. Conclusion

This research presents a detailed exploration and advancement of composite-based biosensors specifically designed for the dual applications of glucose sensing and AF-B_1 detection. Through a methodical progression from initial structural and compositional analyses to final sensor applications, several key insights and developments have emerged which demonstrate the effectiveness and potential improvements of the biosensor systems. A simple electrochemical polymerization method was employed to synthesize the conducting polymer PEDOT-PSS-based nanocomposite using a three-electrode setup. PANI was synthesized through chemical oxidative polymerization of the aniline monomer. Furthermore, PANI-PVA composite nanofibers were successfully prepared using a facile electrospinning technique, discussed in Chapter 2. In Chapter 3, the structural and compositional analysis of the fabricated electrodes was comprehensively examined. The presence of characteristic peaks corresponding to PEDOT-PSS, GO, WS_2, Au, ITO, PANI, and PVA was confirmed through XRD analysis. Furthermore, the existence of functional moieties and vibrational modes within the synthesized composite materials was validated by FTIR. FESEM micrographs of AuNP/GO/PEDOT-PSS and AuNP/WS_2/PEDOT-PSS electrodes offered a testimony to the uniform deposition of Au nanoparticles over the polymer composite films, while EDX further validated the presence of PEDOT-PSS, GO, Au, and WS_2 in both PEDOT-PSS-based hybrid systems. Additionally, FESEM images of the PANI-PVA composite system revealed the formation of a dense network of uniform nanofibers. Electrochemical characterization of the electrodes indicated enhanced charge transfer kinetics in the hybrid PEDOT-PSS-based systems containing AuNPs, as compared to their pristine counterparts, as confirmed through both CV and EIS analyses. These findings demonstrate the superior electrochemical performance of the AuNP-modified hybrid electrodes. Further, the electroactive surface area of all the synthesized electrodes have been evaluated by varying scan rate in CV. This established a foundational

understanding of how the inclusion of gold nanoparticles can elevate the electrochemical performance of hybrid electrodes.

Glucose Sensing and Aflatoxin B_1 Detection (Chapters 4-6)

In chapter 4, a composite biosensor based on an AuNP/GO/PEDOT-PSS (system-I) was developed for two different applications: glucose sensing and AF-B_1 sensing. In both sensing methodologies, the electrodes were functionalized with glutaraldehyde prior to immobilization of biomolecules. The fabricated glucose sensor demonstrated a fast response towards glucose oxidation, with remarkable selectivity and a low LOD of 2.33 µM, effectively detecting glucose within the concentration range of 8.34 to 373.33 µM. For AF-B_1 detection, two distinct immunosensors were prepared. The first, immobilized with mouse IgG to detect mouse derived anti-AF-B_1, exhibited high selectivity and sensitivity across a concentration range of 18.18 to 291.42 ng mL^{-1}, with LOD values of 67.75 ng mL^{-1} at 77 Hz and 62.5 ng mL^{-1} at 1 kHz, as determined from transient capacitance measurements. The second immunosensor, immobilized with anti-AF-B_1 antibodies, achieved high selectivity and sensitivity within a broader concentration range of 18.18 to 300 ng mL^{-1}, yielding LOD values of 55.41 ng mL^{-1} (357 pM) at 77 Hz and 62.45 ng mL^{-1} (402 pM) at 1 kHz. Additionally, DPV analysis of the AF-B_1 sensor revealed a sensitivity of 2.111 µAng^{-1}mL, with an LOD of 65.49 ng mL^{-1} (422 pM) over a detection range of 18.18 to 342.85 ng mL^{-1}. Despite their strong performance, the primary limitation of these biosensors lies in their moderate LOD and sensitivity. In chapter 5, we have improved the sensing parameters by replacing GO with WS_2. The developed AuNP/WS_2/PEDOT-PSS (system-II) composite-based biosensor exhibited significant improvements over the GO based system for both glucose sensing and AF-B_1 detection. The glucose sensor demonstrated a lower LOD of 1 µM, allowing for effective detection within a concentration range of 0.74 to 440.67 µM. The enhanced sensitivity reflects the synergistic effects of WS_2 in combination with AuNPs and PEDOT-PSS. The developed immunosensor for AF-B_1 detection demonstrated excellent selectivity and sensitivity, effectively detecting AF-B_1 within a concentration range of 7.69 to 324.32 ng mL^{-1}, as determined through transient capacitance measurements at both 77 Hz and 1 kHz. The LOD for this sensor was calculated to be 30.97 ng mL^{-1} (206 pM) at 77 Hz and 31.40 ng mL^{-1} (209 pM) at 1 kHz. DPV analysis also displayed a sensitivity of 9.55 µAng^{-1}mL, with an LOD of 37.87 ng mL^{-1} (252 pM) over a concentration range of 18.18 to 325.04 ng

mL^{-1}. Although the biosensor demonstrates improved performance, a key limitation is its relatively moderate dynamic range. In chapter 6, we developed PANI-PVA nanofiber based biosensor (system-III) in order to detect glucose and AF-B_1 sensing. The glucose sensor demonstrated a rapid response to glucose oxidation, with excellent selectivity in presence of many interfering species with a LOD of 1.65 µM, effectively detecting glucose within a wide concentration range of 0.19 to 455.52 µM. The AF-B_1 detection using this sensor exhibited even greater sensitivity, with LODs of 12.82 ng mL^{-1} (85 pM) at 77 Hz and 18.57 ng mL^{-1} (128 pM) at 1 kHz, coupled with a remarkable sensitivity of 11.49 $\mu Ang^{-1}mL$ within a concentration range of 3.92 to 445.76 ng mL^{-1} evaluated through transient capacitance. Additionally, DPV analysis offered a sensitivity as high as 11.49 $\mu Ang^{-1}mL$ $\mu Ang^{-1}mL$, and with an LOD of 17.85 ng mL^{-1} (119 pM) over the same detection range of 3.92 to 445.76 ng mL^{-1}.

Across the chapters, the transition from the AuNP/GO/PEDOT-PSS composite to the AuNP/WS_2/PEDOT-PSS and finally to the PANI-PVA composite demonstrate how choice of different nanocomposites can profoundly optimize sensor performance. The key parameters for each system are tabulated in Table 7.1 (Glucose sensor) and Table 7.2 (AF-B_1 sensor). The ability of the sensors to distinguish glucose in presence of ascorbic acid, uric acid and sucrose; and AF-B_1 even in the presence of non-specific proteins such as BSA and human serum IgG further validates their specificity and practicality for real-world applications. The complementary techniques of transient capacitance and DPV provided reliable measurements, demonstrating the versatility and robustness of the fabricated sensors.

Table 7.1. Detection of glucose was carried out via chronoamperometry.

System	Sensor material	LOD (µM)	Sensitivity ($\mu A\ mM^{-1}$)	Linear range (mM)
I	AuNP/GO/PEDOT-PSS	2.33	10.59	$(3.84\text{-}373.33)\times10^{-3}$
II	AuNP/WS_2/PEDOT-PSS	1	13.1	$(0.74\text{-}440.67)\times10^{-3}$
III	PANI-PVA nanofibers	1.65	11.7	$(0.19\text{-}455.42)\times10^{-3}$

Table 7.2. Detection of Aflatoxin B_1 carried out via Transient capacitance and DPV.

System	Sensor material	Method	LOD (ng mL^{-1})	Sensitivity	Linear concentration range (ng mL^{-1})
I	AuNP/GO/ PEDOT-PSS	Transient capacitance	55.41 (77 Hz) & 62.45 (1 kHz)	6.76 nFng^{-1}mL (77 Hz) & 12.40 nFng^{-1}mL (1 kHz)	18.18-300 (77 Hz) & 18.18-291.42 (1 kHz)
		DPV	65.29	2.112 µAng^{-1}mL	18.18-342.85
II	AuNP/WS_2/ PEDOT-PSS	Transient capacitance	30.97 (77 Hz) & 31.40 (1 kHz)	45.62 nFng^{-1}mL (77 Hz) & 6.60 nFng^{-1}mL (1 kHz)	7.69-324.32 (77 Hz) & 7.69-313.72 (1 kHz)
		DPV	37.87	9.55 µAng^{-1}mL	7.69-325.04
III	PANI-PVA nanofibers	Transient capacitance	12.82 (77 Hz) & 18.57 (1 kHz)	25.64 nFng^{-1}mL (77 Hz) & 21.27 nFng^{-1}mL (1 kHz)	3.92-445.76 (77 Hz) & 3.92-445.76 (1 kHz)
		DPV	17.85	11.49 µAng^{-1}mL	3.92-445.76

Further, the effective validation of these sensors using human saliva samples (for Glucose) and mushrooms, okra, and peanuts (for AF-B_1) demonstrates their practical utility in real-life circumstances, enhancing their appeal for non-invasive monitoring and food safety applications respectively. In summary, the results confirmed the effectiveness of combining conducting polymers, 2D materials, and gold nanoparticles for fabricating high-performance electrochemical biosensors. These sensors demonstrated great potential for practical applications in glucose monitoring and food safety, offering a promising path for the future development of biosensing technologies aimed at improving human health and safety of foodstuffs.

7.2. Future outlook

Overall, this study highlights the continuous improvement in the design and functionality of biosensors through innovative composite materials. Despite their strong performance, the sensors still face challenges in terms of its characteristic parameters, which warrant further research and optimization. Future efforts could focus on fine-tuning material compositions, exploring novel nanomaterials, and enhancing the dynamic range of biosensors to meet the demands of diverse applications. The findings herein not only contribute to the field of biosensing but also open avenues for further exploration into more efficient and effective sensing technologies.

(i) The sensing performance can be significantly improved by using novel material MXenes, which provide an exceptionally high surface area and excellent conductivity, making it ideal for catalytic applications.

(ii) Use of EDC-NHS (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide/N hydroxysuccinimide) in place of glutaraldehyde may add value to the sensing activity.

(iii) A 2D-2D heterostructure, such as the combination of graphene oxide (GO) and tungsten disulfide (WS_2) can offer synergistic effect on the sensor performance.

(iv) GO or exfoliated TMDC materials can be opted with PANI-PVA nanofibers. Use of metal nanoparticle with nanofiber system may also augment values in electrochemical sensing.

(v) The effect of different enzyme loadings on the sensor surface can be explored to optimize its performance for glucose detection.

(vi) To validate the accuracy of the developed glucose sensor and extraction method, conventional saliva glucose assays can be conducted.

(vii) The synthesized materials can be explored for the detection of various types of aflatoxins, expanding the scope of their application in food safety and quality assurance.

(viii) In the future, the sensing probe can be developed as a compact portable device for fast and reliable sensing. This can be achieved by utilizing Arduino circuits and programming them to align with specific experimental conditions and calibration equations.