



Colloidal SnO₂ nanoparticles for the enhancement of PEDOT:PSS-coated string electrodes for potential use for glucose sensing

Bianca Seufert¹ · Sylvia Thomas¹ · Arash Takshi¹

Received: 20 November 2023 / Accepted: 7 March 2024 / Published online: 22 March 2024
© The Author(s), under exclusive licence to The Materials Research Society 2024

Abstract

As the healthcare industry continues to evolve its approach to monitoring patient health, the growing need for rapid accurate biosensing in a wearable device is becoming more and more relevant. Along with size, weight, and various technology constraints, making a nanoscale biosensor can be beneficial in furthering this exploratory venture. In this work, string-shaped electrodes have been fabricated by coating PEDOT:PSS on commercially available threads. Some of the electrodes were further coated with a solution containing SnO₂ nanoparticles. By immobilizing glucose oxidase (GOx) on the strings, the electrodes were electrochemically characterized when they were exposed to the electrolytes containing glucose. The cyclic voltammetry and electrochemical impedance spectroscopy results show that the presence of NPs has a significant effect on electrochemical response of the electrodes particularly after the immobilization of GOx. The chronoamperometry (CA) studies of the two electrodes verify the impact of NPs in the sensitivity of the electrodes reaching 83.70 $\mu\text{A}/\text{mMcm}^2$. The promising results from this work encourage designing wearable sensors with the string-shaped electrodes coated with SnO₂ nanoparticles for future wearable sensors.

Introduction

While many real-world applications can utilize biosensors, the most notable is in health monitoring. This application spans across industries far beyond healthcare and even into space exploration. From monitoring glucose in diabetics to pathogen testing in extreme and remote environments. The need for biosensors is indisputable which is why the need to continuously adapt, develop, and fine tune the sensitivity, flexibility, and overall durability of biosensors is so imperative. Moreover, given this critical need researchers are turning towards nanoscale technologies to find ways of enhancing existing biosensing technologies. This can be seen most notably in the development of glucose sensors.

Historically, glucose sensors have strictly utilized blood to monitor the illness known as diabetes [1]. This invasive testing method can be uncomfortable, to say the least, and an alternative (i.e., non-invasive approach) would be a relief

to many diagnosed diabetics. Furthermore, not only would it be beneficial to have a non-invasive test method, such as a sweat testing glucose sensor, but also a wearable one for continuous sensing throughout the day as diabetics must monitor their glucose levels periodically [2]. In order to meet this challenge, many researchers are looking at a variety of nanomaterials to meet this need such as but not limited to implementing carbon-based nanomaterials [3], conductive polymer-based nanofibers [4], and metal/metal-oxide-based nanoparticles for thin-film enhancements on biosensors [5].

Moreover, given the versatility and freeform movement metal-oxide nanoparticles provide to flexible substrates, it is no wonder why researchers are exploring the addition of these helpful nanomaterials. SnO₂ nanoparticles have attracted a lot of interest in this area due to their non-toxicity, advantageous catalytic activity, and preferable chemical stability [6]. For example, three different research groups applied SnO₂ nanoparticles to the surfaces of glassy carbon electrodes [5], graphene mat [7], and tin-oxide nanosheets [8] for increased sensitivity in biosensor applications. Given the beneficial electrochemical and electrocatalytic properties that were observed, the enhanced sensitivity outcome these nanoparticles have on interfacing with electrons for an accelerated transfer can be deduced. In each of these

✉ Bianca Seufert
bseufert@usf.edu

¹ Department of Electrical Engineering, University of South Florida (USF), 4202 E. Fowler Ave, Tampa, FL 33620, USA

reported studies, the nanoparticles were adsorbed to the surface without linker molecules and therefore it stands to reason that this method could be extended to other substrates such as polymer-based conductive coatings on completely flexible string threads. The addition of these nanoparticles along with allowing for movement from the substrate also add to the surface area of the substrate for more interaction with the target analyte, as seen in the reported works listed above, to facilitate a desirable effect when interacting with the active site of enzyme-based biosensors.

This overall approach could provide further advancement into biosensor applications for wearable scenarios such as patient gown health monitoring with sewn-in biosensors. Given that new and exciting research, such as this, is being undertaken everyday it is exciting to see how the advancement of this field continues to unfold. Furthermore, in this work, we have studied the effect of adding SnO₂ nanoparticles (NPs) to a string-shaped electrode intended for glucose sensing. The results verify the improvement in the sensitivity of the electrode with the SnO₂ NPs versus the electrode without any NPs coating.

Materials and methods

Materials

The dodecylbenzenesulfonic acid (DBSA), ethylene glycol (EG), Tin(IV) Dioxide (SnO₂) nanoparticle ink (2.5w.% 3.5cP), high-conductivity grade PEDOT:PSS (4% in H₂O),

D-Glucose (180.16 g/mol), and potassium ferricyanide (329.26 g/mol) were all from Sigma-Aldrich. The glucose oxidase (GOx), glucose enzyme, was from Aspergillus Niger. The 25% Cotton + 75% Polyester-blended string was purchased from Walmart.

Experimental procedure

Two different electrodes were fabricated for this work. The base of each electrode was made up of the commercially available 25% Cotton + 75% Polyester-blended string. A conductive PEDOT:PSS-based coating solution was created by mixing PEDOT:PSS, DBSA, and EG with the 75:20:5 mass ratio following a recipe developed in our lab [9]. To create each string electrode, the following procedure was applied [10]. Firstly, 3-cm-long string of the 25% Cotton + 75% Polyester thread was cut. Then each string was individually submerged in the PEDOT:PSS coating solution. After 30 min, the strings were removed and left to dry for 6–8 h. This coating process was repeated twice for each string turning them into the basis for the string electrodes.

From there 5 μ L of SnO₂ ink was drop casted onto one of the PEDOT:PSS-coated string electrodes which will be referred to as the SE-SnO₂ electrode. According to the supplier, the average size of the nanoparticles was 7–20 nm in diameter and could not be seen using the SEM therefore they have been enlarged in the diagram of Fig. 1 for reference. Another 3-cm-long electrode without any NPs coating was fabricated, and will be referred to as SE-P. This electrode was used as a controlled sample to be compared with the

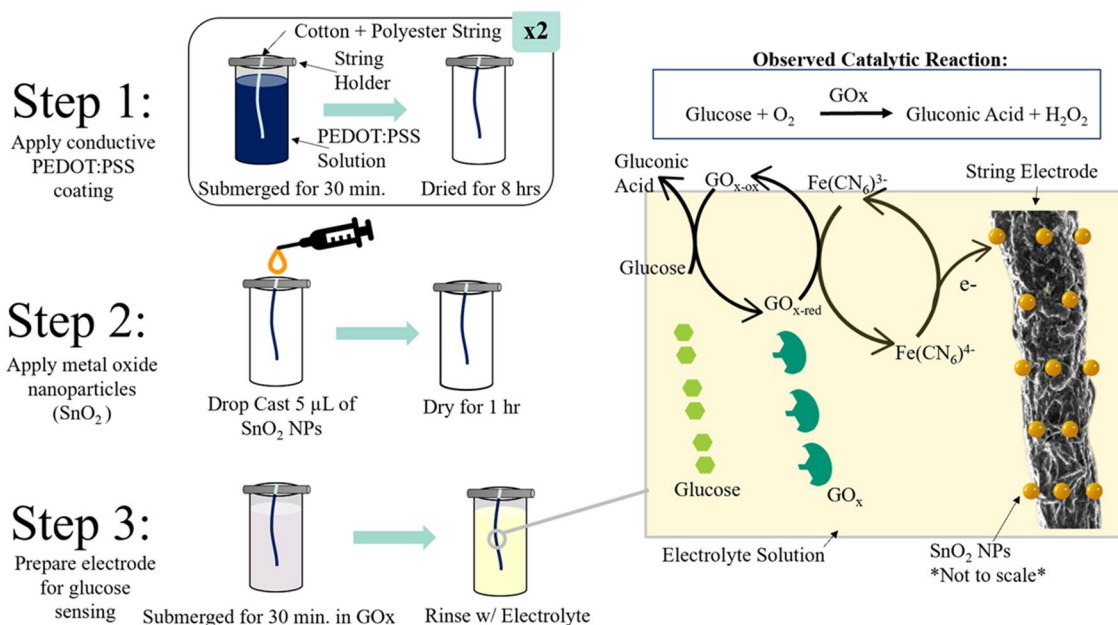


Fig. 1 Experimental procedure for preparing each electrode with diagram of the chain reactions occurring at the surface of the electrode

electrode with the NPs. Following the recipe from [9], once finally dried each electrode was individually submerged in 100 μ L GOx enzyme solution, 50 mg/mL ratio in distilled water, for a minimum of 30 min at 4 °C to immobilize the enzymes onto the surface of the two electrodes (i.e., with and without NPs). Afterward, the electrodes were rinsed with electrolyte solution to remove excess.

For the electrochemical experiments, a beaker was used to encase the electrochemical cell with a silver/silver chloride (Ag/AgCl) reference electrode (RE) and a platinum wire as the counter electrode (CE). Following the recipe from [11], the electrolyte solution, with a pH of 7.2, was prepared using a 1:1 ratio of 5 mM potassium ferricyanide added to sodium acetate buffer solution. Up to 1.0 M glucose in deionized water was used for creating various glucose–electrolyte ratios. The cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronoamperometry measurements were carried out using a VersaSTAT 4 Potentiostat. A 50 mV/s scan rate over a span of 5 cycles was implemented for the CV tests, however, only the third cycle of each experiment is presented in this work. A frequency range of 0.01 Hz–1 kHz with an amplitude of 50 mV was applied for the EIS tests. 0.5 V was applied to the working electrode for the chronoamperometry test which was then used to monitor the current as varying amounts of diluted glucose solution were added to the electrolyte every 30 s. The SU-70 Hitachi Scanning electron microscope (SEM) was used to obtain images of the string electrode surfaces.

Results

Given the work reported in [9], the results have shown that 25% Cotton + 75% Polyester-blended string has a better conductivity than other commercial tested threads when being coated with PEDOT:PSS. Furthermore, it seemed beneficial to utilize this result and implement the 25% Cotton + 75% Polyester-blended string as the base string to be coated. The 25% Cotton + 75% Polyester-blended string is made up of aligned twisted fibers with an average fiber diameter of roughly 15 μ m and an overall diameter of around 270 μ m. The SEM image in Fig. 1 clearly shows that the PEDOT:PSS coating is somewhat uniform and can optically be considered coated.

Figure 2 shows the CV and EIS responses of the string electrodes. Firstly, the “baseline” response of each electrode is defined as being electrochemically tested without any glucose or glucose enzyme present during testing. Secondly, after the electrodes were exposed to the GOx enzyme they were tested which is defined as the “enzyme” response. Lastly, once the electrode’s “enzyme” response was captured they were electrochemically tested in 1:1 electrolyte

of 0.5 M glucose and buffer solution which was defined as the “glucose” response.

The electrochemical responses of the electrodes to varying amounts of glucose were further studied using a chronoamperometry experiment. Figure 3 shows the responses of both electrodes to the addition of glucose to the electrochemical cell increasing the concentration by 3 mM of glucose at each addition to the solution over time. During the chronoamperometry testing period it was observed that some of PEDOT:PSS coating was starting to seep into electrolyte solution from the string electrodes as the normally yellow solution started to turn a blueish green color. This could possibly be due to the adsorption of the electrolyte within the string. This also highlights why the consistency in response to glucose could not be maintained at the surface of each string electrode over time.

Discussion

As seen in Fig. 2, there are defined peaks for each string electrode elaborating upon the reactions occurring at the electrode’s surfaces. From the CV results in Fig. 2a, it is evident that the double-layer capacitive behavior of the SE-P electrode is dominant in all three of its loops. The baseline CV loop from the SE-SnO₂, Fig. 2c, is considerably smaller showing a less capacitive behavior. Also, in the baseline, the SE-SnO₂ shows a small oxidation peak at around +0.2 V, and it does have a small reduction peak around –0.5 V. However, after the enzyme immobilization, a much larger loop appeared in the CV results, particularly in the negative voltage range. Additionally, a new set of reduction peaks appeared while limiting the oxidation peaks confirming that the immobilized GOx can effectively interact with the string electrodes. The peak shifted after introducing glucose to the electrolyte. It should be noted that due to the capacitive response of the SE-P electrode (Fig. 2a), the redox peaks are weaker than those in the SE-SnO₂ string electrode (Fig. 2c).

Furthermore, the electron transfer nature of each electrode can be seen in the EIS results presented in Fig. 2. While the low-frequency tails in the EIS of the SE-P in Fig. 2b suggest domination of diffusion, the semicircle shape of the EIS for the SE-SnO₂ string in Fig. 2d emphasizes the domination of the electron transfer rate, which as shown in Fig. 1 is only limited by the slowest reaction in the reaction chain between glucose and the electrode’s surface. Moreover, the results from Fig. 2d show that after immobilizing GOx, the electron transfer was improved, this can be further confirmed by knowing the diameter of the semicircle (R_{ct}) is inversely proportional to the electron transfer rate [12]. However, we do observe a reduction in the electron transfer across both string electrodes when glucose was introduced to the electrolyte.

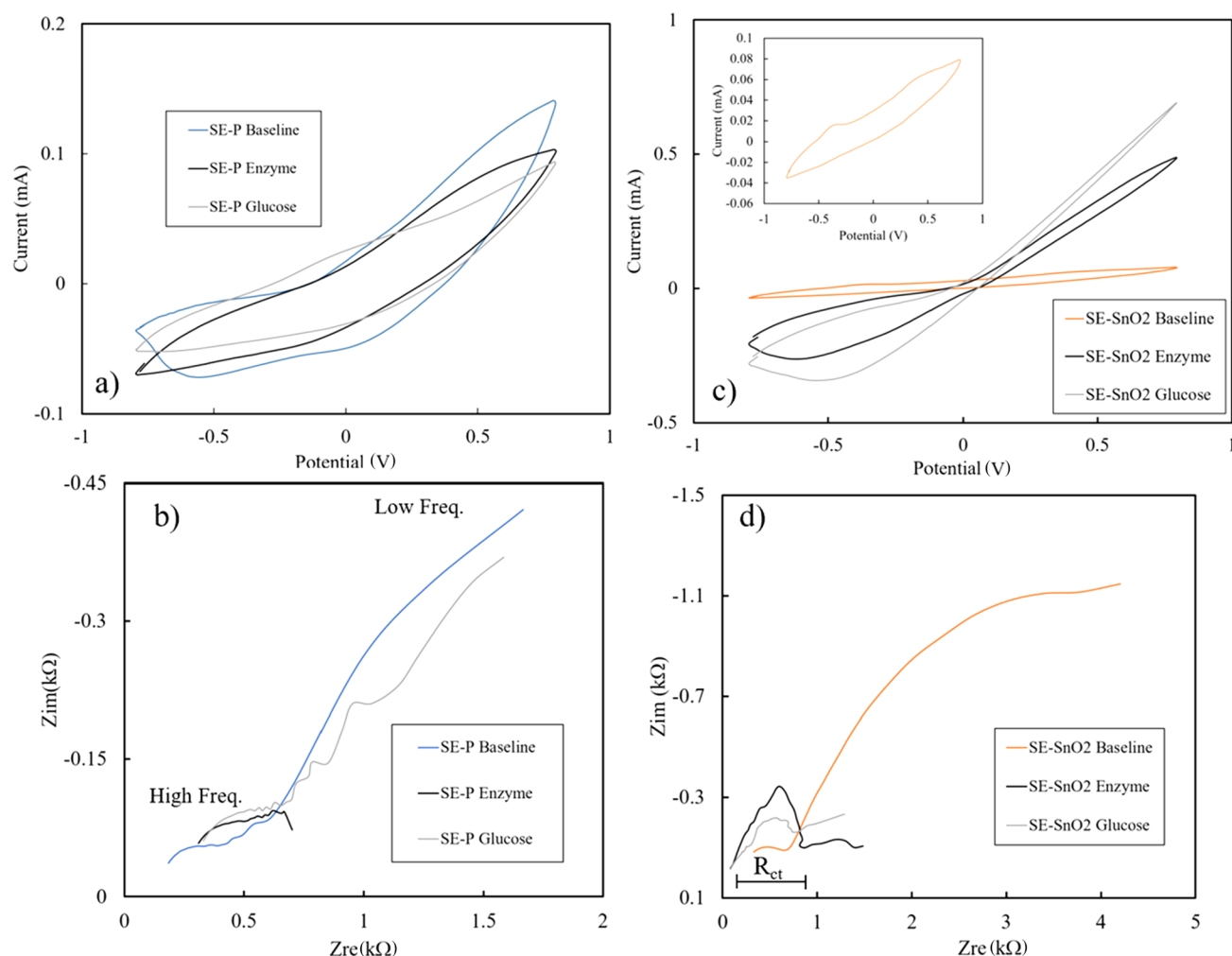


Fig. 2 **a** CV and **b** EIS results for SE-P electrode and **c** CV and **d** EIS results for SE-SnO₂ electrode

As seen in Fig. 3, the SE-P electrode has a 3s response time with a 1.2 μ A increase after each additional drop of the glucose solution, however, as time progresses the response time lengthens to 4 s along with an increase in response at 1.5 μ A. A similar effect in response time is seen in the SE-SnO₂ with a 3s response but with a much larger current response overall starting with 10 μ A and increase to 0.11 mA. Overall, while response time for all sensors was relatively the same for the given time period studied, it can be seen that the SE-P electrode remained the least variable long term and the SE-SnO₂ electrode showed the highest increase in response.

Moreover, in Fig. 3b and d, the linear regression calibration curves were calculated for each string electrode based off the observed chronoamperometry results. From there the sensitivity could be calculated, slope of calibration curve divided by the total surface area of the electrode as done in [11], and the limit of detection (LOD), derived from the fitted linear curve and its slope as seen

in Fig. 3. These values are presented in Table 1. As can be seen, the resulting sensitivity of SE-SnO₂ is more than 13 times more sensitive than that of the SE-P electrode demonstrating the benefit of the addition of the SnO₂ NPs. In comparison, Table 1 also lists a few of the recent research efforts regarding the study of flexible electrodes for electrochemical glucose biosensing and compares the results to this work. As is further demonstrated in Table 1, SE-SnO₂ electrode showed the highest sensitivity among other reported results using fiber-based electrodes. Although the LOD in the SE-SnO₂ is an order of magnitude better than the SE-P electrode, other reported results have significantly lower LOD than our samples. Nevertheless, the high sensitivity with SnO₂ nanoparticles clearly shows the effect of the NPs on the biosensing capability of the PEDOT:PSS-coated electrodes. Further studies are planned to learn about the effect of density and size of the NPs on the biosensing capabilities of the electrodes.

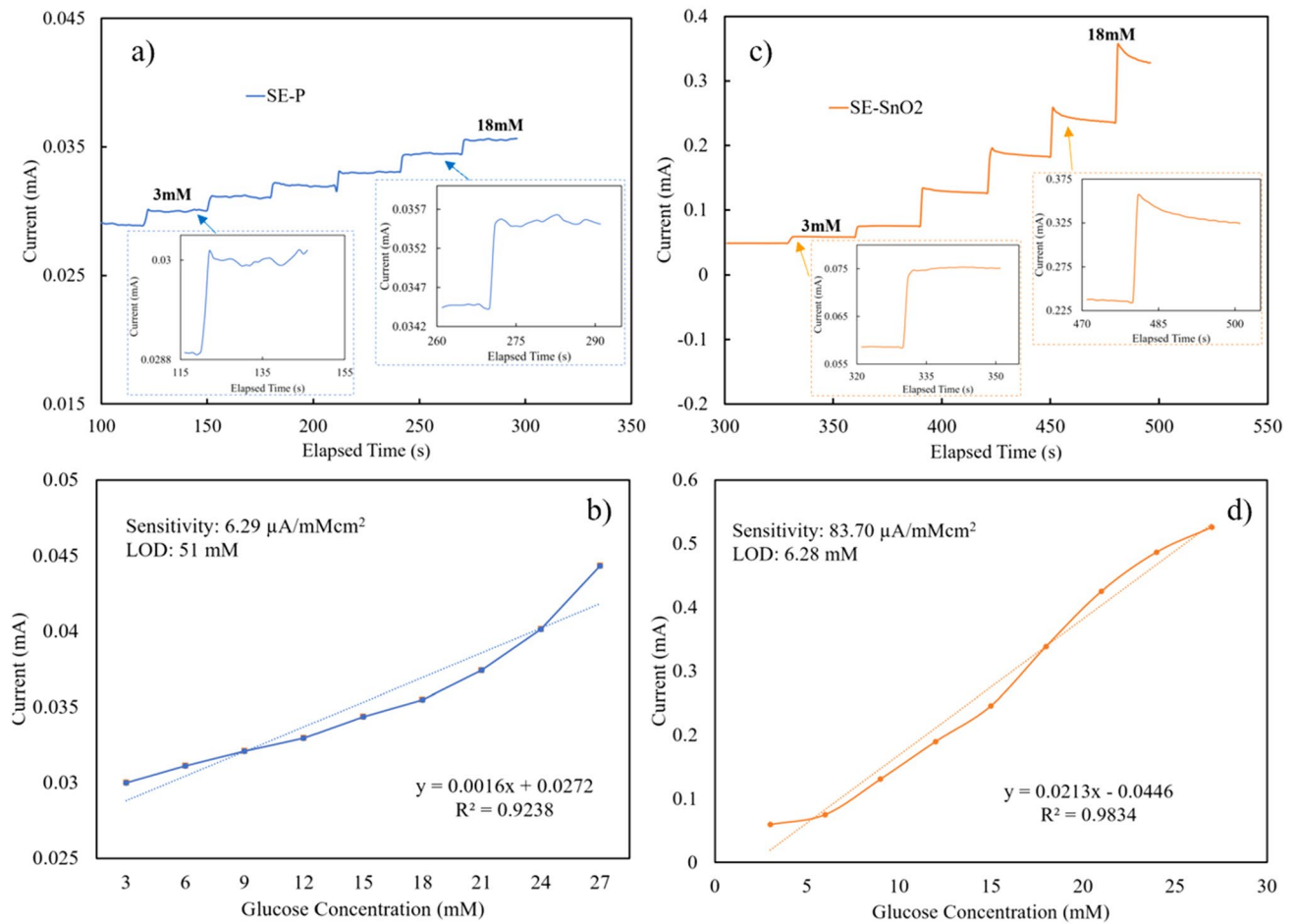


Fig. 3 Chronoamperometry test results for **a** SE-P, **c** SE-SnO₂, **b** Δ Current vs Glucose response for SE-P, **d** Δ Current vs Glucose response for SE-SnO₂

Table 1 Summary of reviewed works in comparison to this work

Reference	Sensing electrode	Sensitivity	Limit of detection	Concentration range
Aleeva et al. [4]	Pt/PEDOT-NFs/GO _x	$9.2 \mu\text{A}/\text{mM cm}^2$	0.26 mM	0.1–25 mM
Puttananjegowda et al. [11]	Au/PEDOT:PSS-PVDF-ENFM/GO _x	$5.11 \mu\text{A}/\text{mM cm}^2$	2.3 μM	0–25 mM
Cetin and Camurlu [13]	PEDOT-NFs/Gox-3	$74.22 \mu\text{A}/\text{mM cm}^2$	2.9 μM	0–4.5 mM
This work (SE-P)	25% cotton + 75% polyester/PEDOT:PSS	$6.29 \mu\text{A}/\text{mM cm}^2$	51 mM	0–27 mM
This work (SE-SnO ₂)	25% cotton + 75% polyester/PEDOT:PSS/SnO ₂ NPs	$83.70 \mu\text{A}/\text{mM cm}^2$	6.29 mM	0–27 mM

Conclusions

In conclusion, a 25% Cotton + 75% Polyester-blended string, coated with a PEDOT:PSS-based conductive coating, was used as a base to fabricate flexible string electrodes. The electrode was then enhanced with the implementation of a colloidal metal-oxide nanoparticle ink SnO₂. The results show that the presence of NPs directly impacts the direct electrode interfacing with the

electrolyte. While the non-enhanced string electrode's response, SE-P, was dominated by diffusion of ions, a double-layer charge at the electrode–electrolyte interface was seen. The electron transfer process can be directly correlated to glucose detection which can be promoted by the nanostructure of the nanoparticles present at the surface of an electrode as was seen in the SE-SnO₂ electrode's CV and EIS responses. Furthermore, it is important to address that overall, the SE-SnO₂ electrode provides a more obvious response to the addition of glucose within

the electrolyte over time, while the SE-P electrode had the least amount of variability overall during the chronoamperometry testing. The findings found from this work contribute to the development of flexible electrodes utilizing colloidal metal-oxide-based nanoparticle solutions for the advancement of biosensor research.

Author contributions BS is the first author and corresponding author for this work and can be reached at bseufert@usf.edu. AT and ST were editors of this work.

Funding Bianca Seufert received support from NSF FGLSAMP BD: University of South Florida Florida-Georgia Louis Stokes Alliance for Minority Participation (FGLSAMP)—HRD # 1906518.

Data availability Data will be made available upon request.

Declarations

Conflict of interest All authors claim no conflicts of interest.

References

1. L. Tang et al., *Sensors* (Basel) (2020). <https://doi.org/10.3390/s20236925>
2. H. Zafar et al., *Sensors* (Basel) (2022). <https://doi.org/10.3390/s22020638>
3. A. Qureshi, J.H. Niazi, *Mater. Horiz.* (2023). <https://doi.org/10.1039/d2mh01517j>
4. Y. Aleeva et al., *IEEE Sens. J.* (2018). <https://doi.org/10.1109/jsen.2018.2831779>
5. S. Alim et al., *Int. J. Biol. Macromol.* (2019). <https://doi.org/10.1016/j.ijbiomac.2018.11.171>
6. J. Chen et al., *Appl. Catal. B* (2023). <https://doi.org/10.1016/j.apcatb.2022.122350>
7. Q. Zhou et al., *Biosens. Bioelectron.* (2013). <https://doi.org/10.1016/j.bios.2013.04.037>
8. A.K.M. Kafi et al., *JNN*. (2021). <https://doi.org/10.1166/jnn.2021.19283>
9. N.O. Marquez Rios et al., *Organic and Hybrid Sensors and Bioelectronics XVI* (SPIE, Bellingham, 2023). <https://doi.org/10.1117/12.2677536>
10. B. Seufert et al., *Sensors* (2024). <https://doi.org/10.3390/s24041283>
11. K. Puttananjegowda, A. Takshi, S. Thomas, *Sens. Lett.* (2020). <https://doi.org/10.1109/lensens.2020.2971515>
12. P. Bollella, E. Katz, *Sensors* (Basel) (2020). <https://doi.org/10.3390/s20123517>
13. M.Z. Cetin, P. Camurlu, *RSC Adv.* (2018). <https://doi.org/10.1039/c8ra01385c>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.