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Cobalt-Based Ferrite Modified Carbon Nanotubes Fibers for Flexible and Disposable Microelectrode Toward Electrochemical Glucose Sensing

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ABSTRACT

Glucose detection is critical in clinical health and the food industry, particularly in the diagnosis of blood sugar levels. Carbon-based fiber materials have recently featured prominently as non-enzymatic electrochemical glucose detectors. Herein, cobalt-based ferrite ($CoFe_2O_4$) in the form of nanoparticles has been successfully fabricated over the carbon nanotubes (CNTs) fiber via a simple hydrothermal process. Fabricated microelectrode ($CoFe_2O_4$@CNTs) was investigated as an electrocatalyst toward the non-enzymatic electrochemical glucose sensors. The structure and morphology of the modified fiber were studied by scanning electron microscopy including energy-dispersive X-ray spectroscopy. The electrochemical capability of the microelectrode was analyzed by using different electrochemical techniques including cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy (EIS). The proposed sensors exhibited a superb sensitivity of 0.21 μAcm^{-2} mM^{-1}, a good linear range from 1 to 9 mM, and a lower detection limit of 1.7 mM. Further investigation via EIS indicated the low charge transfer resistance as compared to the bare CNTs-based fiber. Outcomes revealed that the material can potentially prove promising for the disposable microelectrode toward electrochemical glucose sensing.

1 | Introduction

In recent years, the percentage of diabetic patients has been rising quickly all over the world. Diabetes can cause serious issues such as renal failure, cardiovascular disease, and blindness. According to the World Health Organization, diabetes will be the seventh most fatal disease by 2030 [1]. To this end, continuous monitoring of blood glucose levels is vital to overcome the chronic stage. Multiple technologies have been used to detect glucose concentration including spectrophotometers [2], mass

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spectrometry [3], fluorescence [4], and electrochemical sensors [5]. Electrochemical-based measurements including both enzymatic and non-enzymatic sensing are fascinating for the detection of glucose due to their improved sensitivity, quick response time, and better selectivity [6]. For blood glucose sensing, initial glucose sensors were commonly based on the glucose oxidase enzyme [7]. Owing to the intrinsic nature of enzymes, they lose their catalytic activity at high temperature and pH [8]. Thus, enzyme-free glucose sensors were presented as promising and facile alternatives due to their significant benefits such as outstanding stability, low cost, higher sensitivity, and simple fabrication process [9].

For electrochemical detection of glucose, electrode material plays a critical role in optimizing sensor domains like sensitivity and detection limit. So far, different classes of materials have been utilized including transition metals, their oxides, polymer, and carbon-based materials [10]. Ternary metal oxides with two distinct metal cations have gained much interest in current years as compared to binary transition metal oxides because of their potential applications in batteries [11], supercapacitors [10d, 12], and sensors. No doubt, the metal and their derivatives have much potential for catalytic applications in different directions but still, there is a gap in terms of stability, activity and selectivity.

Cobalt-based ferrite ($CoFe_2O_4$) has attracted significant interest for a variety of potential applications, including semiconductor photocatalysts [13], sensors [14], cancer therapy [15], biomedical [16], optical behavior [17], electrical [18], and antibiotic functions [19]. In contrast to Fe_2O_3 and Co_3O_4, $CoFe_2O_4$ sensor material exhibits better electro-catalytic activity [20]. Additionally, $CoFe_2O_4$ has a number of exciting benefits as compared to other materials including their low cost, better electrocatalytic activity, good biocompatibility, high capacity, and facile preparation. As a result, $CoFe_2O_4$-based non-enzymatic glucose sensing materials with improved performance, including sensitivity, reliability, and reaction time, will have a promising future.

Carbon-based materials including CNTs [21], carbon cloth, and graphene [22] have been extensively probed to improve the detection performance of sensors with high surface area and excellent conductivity. However, carbon-based materials do have not sufficient active sites which hinders these materials from performing better. In order to overcome the drawbacks, researchers focused their interest on flexible materials with porous channels and high electrical conductivity [23]. Shuang Dong et al. synthesized a flexible carbon fiber-based microelectrode wrapped with reduced graphene oxide loaded Ni-MOF array. This electrode showed a sensitivity of 852 μA mM^{-1} cm^{-2}, a detection limit of 0.6 μM, and a wide linear range of 6 μM–2.09 mM [24]. Mari Elancheziyan et al. fabricated a graphitic porous carbon nanohybrid composite, which showed lower charge transfer resistance and high ionic diffusion. A prepared composite displayed a lower detection limit of 7.8 μM and a wide linear range from 0.03 to 1.07 mM [25]. In contrast to carbon-based fiber, high alignment and twisting arrangements in flexible CNT fiber exhibit high tensile strength and provide a long path for charge transport. Hence flexible CNT fiber, currently accepted as an excellent material with multi-porous channels, displays a better flow of charges to increase the overall performance of the electrode [26].

Flexibility of the electrode materials is another advancement for wearable sensors. For this purpose, numerous efforts have been made on various textile-based materials including carbon clothes [27] and other modified flexible substrates [28]. To this end, we have synthesized cobalt-based ferrites ($CoFe_2O_4$) nanoparticles by hydrothermal process and used these nanoparticles as electrocatalysts for the electrochemical detection of glucose. The shape and structure of $CoFe_2O_4$ nanoparticles were examined using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis. Densely populated CNT fibers, with each entity, provide a higher mechanical strength, whereas $CoFe_2O_4$ nanoparticles deposited over CNT fiber initiate the catalytic oxidation for glucose. The electrocatalytic activity of fabricated electrode $CoFe_2O_4$@CNTs fiber was examined, using various electrochemical techniques such as cyclic voltammetry, chronoamperometry, and impedance spectroscopy. The fabricated electrode exhibited a remarkable sensitivity of 21 μA mM^{-1} cm^{-2}, a lower detection limit of 1.7 mM, and a linear range of up to 9 mM. This fabricated microelectrode (CNTs@$CoFe_2O_4$) could prove an attractive material for applications in wearable and flexible electrochemical biosensing. (Figure 1 shows the schematic illustration for the electrochemical oxidation of glucose at the surface of modified CNTs fiber, i.e., $CoFe_2O_4$@CNTs).

2 | Experimental Section

2.1 | Materials

The chemical reagents including glucose, potassium hydroxide (KOH), Ferrous sulfate ($FeSO_4{\cdot}7H_2O$), Cobalt chloride ($CoCl_2{\cdot}6H_2O$), and urea (CH_4N_2O) were purchased from Sigma Aldrich. CNT fibers were prepared via the wet chemical process and were used as received. All the solvents utilized in the experiments were of analytical grade and were used without any further purification.

2.2 | Preparation of $CoFe_2O_4$ Nanoparticles and Electrode Fabrication

The $CoFe_2O_4$ nanoparticles have been synthesized via the hydrothermal method by using ferrous sulfate and cobalt chloride as precursors. Initially, 0.5 mM $CoCl_2{\cdot}6H_2O$ and 1 mM $FeSO_4{\cdot}7H_2O$ were dispersed in 20 mL deionized water (DI). Subsequently, the mixture was sonicated for 30 min after combining with 5 mM urea. The mixture was then transferred into a Teflon-lined corrosion-resistive 25 mL autoclave, which was kept in an electric oven at 160°C for 6 h. After cooling down at room temperature, the product was washed various times with ethanol and water to get rid of any undissolved contaminations and dried at 50°C. For electrode fabrication, a simple drop-casting method has been adopted via slurry formation [29]. Nafion used as binder in the mixture of water and ethanol as a dispersion medium in which as-synthesized material has been dispersing under ultrasonication. With the help of a micropipette, a dope of the slurry has been added over the pre-cleaned CNTs fiber and heated in an oven at 80°C for 1 h prior to use this electrode for electrocatalytic performance.

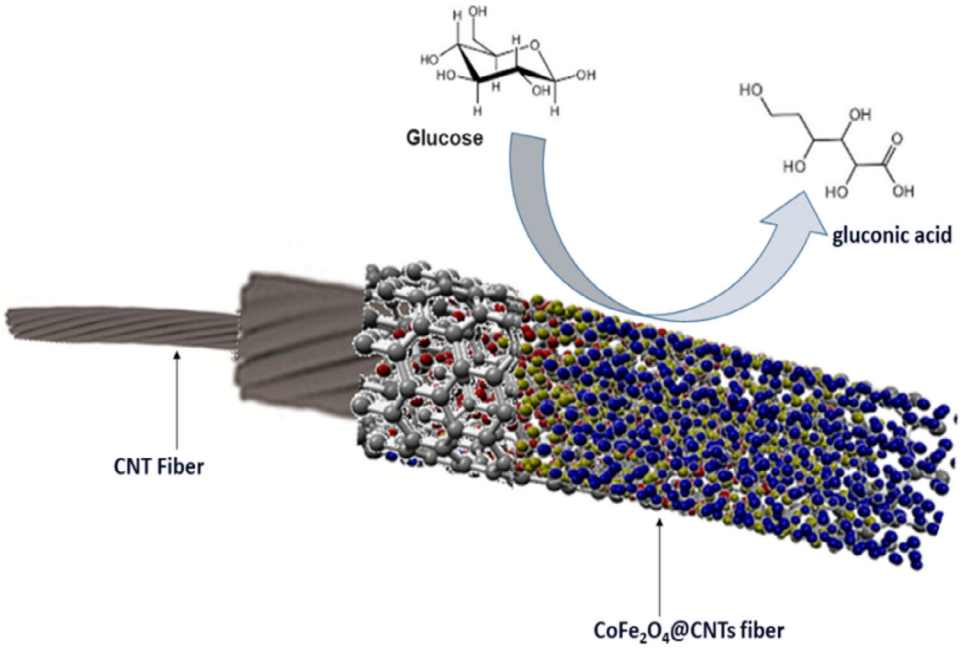

FIGURE 1 | Schematic illustration for the electro-oxidation of glucose over the surface of modified ($CoFe_2O_4$@CNTs) fiber.

2.3 | Electrochemical Measurements and Electrode Fabrication

Electrochemical tests, including cyclic voltammetry, linear sweep voltammetry, chronoamperometry, and EIS were carried out with a Gamry Reference 3000 Potentiostat/Galvanostat/ZRA using the conventional three-electrodes system, where a platinum wire served as the counter electrode, an Ag/AgCl electrode served as a reference electrode and the modified CNTs fiber served as a working electrode in 0.1 M KOH at room temperature. The working electrode was prepared by making a slurry of $CoFe_2O_4$ in DI water and ethanol mixture (at the proportion of 1:1) under sonication for 30 min. Amperometric measurement was performed under continuous magnetic stirring for convective mass transport. Electrochemical impedance spectroscopy was carried out with AC frequency from 0.1 Hz to 1 MHz at 0.6 V DC potential. All electrochemical measurements were performed at room temperature.

3 | Results and Discussion

3.1 | Surface Morphology

SEM was used to obtain information about the structure and morphology of the prepared sample [30]. SEM images of bare CNT fiber at magnifications of 20 and 1 μm are shown in Figure 2. Each individual entity of CNT fiber provides high mechanical strength along with a charge carrier pathway. A unique interconnected aligned structure, as displayed in Figure 2b, has the beneficial impact of providing quite a smooth flow of charges. Apparently, rough surfaces appear in Figure 2c,d at different magnifications (20 and 1 μm), which indicates that a large number of $CoFe_2O_4$ nanoparticles have successfully been deposited and evenly dispersed over the fiber surface. Highly aligned CNT fiber could effectively prevent the agglomeration of $CoFe_2O_4$ and hence extraordinarily increase the exposed active sites of $CoFe_2O_4$.

Elemental composition was examined through EDX as shown in Figure 3. EDX spectrum confirmed the presence of Fe, and Co and clearly elaborated the uniform distribution over the fiber surface. Red mapping shows the dispersion of cobalt in Figure 3e, yellow mapping shows carbon in Figure 3b while the green and light blue mappings show the oxygen and iron in Figures 3c and 3d, respectively. Figure 4 shows the relative abundance of each element deposited over the modified surface of CNT fiber and it was observed that carbon, as a substrate, showed the maximum value in comparison to the deposited iron, cobalt, and oxygen.

3.2 | Electrochemical Studies of $CoFe_2O_4$ for Glucose Sensing

The electrochemical behavior of $CoFe_2O_4$@CNT fiber was examined under 0.1 M KOH solution in the presence and absence of glucose (see Figure 5a). With the addition of 15 mM glucose, modified $CoFe_2O_4$@CNT fiber displayed an oxidation peak in alkaline media at 0.56 V versus Ag/AgCl, confirming that $CoFe_2O_4$@CNTs fiber exhibits excellent electrocatalytic activity. A higher current in cyclic voltammogram (CV) measurement at 0.6 V indicates that $CoFe_2O_4$ overall improved the electrocatalytic activity and boosted the faradic process at the electrode surface. In Figure 5a, the faradic current initiated at 0.5 V and reached the maximum value at 0.6 V versus Ag/AgCl with a reasonable current density of 4 mA/cm^2 value. In the reverse scan, no cathodic peak appeared which represents an irreversible phenomenon at the electrode surface. Additionally, a comparison of the current densities at 1 mM and 15 mM glucose concentrations has been

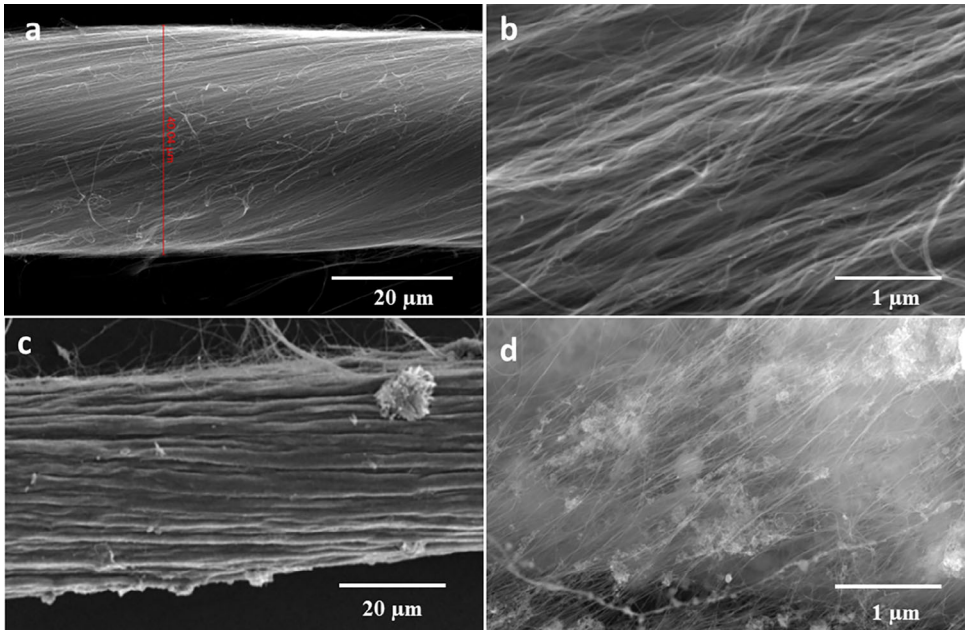

FIGURE 2 | Scanning electron microscopy (SEM) images for bare carbon nanotube (CNT) fiber at (a) 20 µm and (b) 1 µm magnification, and $CoFe_2O_4$@CNT fiber at (c) 20 µm and (d) 1 µm.

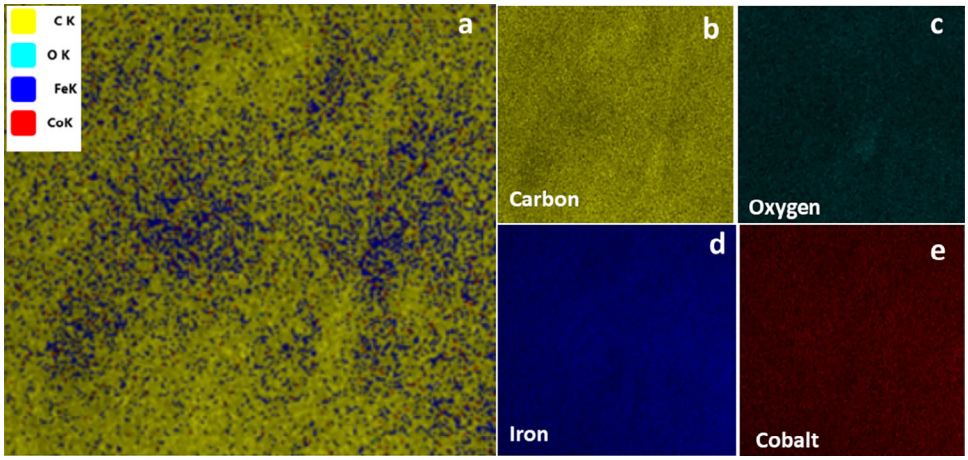

FIGURE 3 | (a) Scanning electron microscopy (SEM) image of $CoFe_2O_4$@CNT and its corresponding energy-dispersive spectra for the elemental X-ray mapping for (b) carbon, (c) oxygen, (d) iron, and (e) cobalt.

provided in Figure 5b. The electrochemical behavior was further explored at the electrode surface by recording voltammograms at various concentrations of glucose in a solution containing 0.1 M KOH, where a fixed scan rate of 50 mV/s was employed to obtain the voltammogram Figure 6a. With the addition of an increasing amount of glucose, oxidation peaks appeared at 0.6 V vs Ag/AgCl while indicating a significant increase in the current densities. Figure 6b illustrates a linear relationship between the current density and the glucose concentration with an R^2 value of 0.99l. It was observed in Figure 6a, that the current response increased linearly with an increase in the glucose concentration from 1 mM to 9 mM with the sensitivity of 0.21 µA mM^{-1} cm^{-2} and further addition led to a linear current response but with lower slope (0.077) and consequently with lower sensitivity (0.077 µA mM^{-1} cm^{-2}) at higher concentration. In order to explore the mass transfer phenomena at the electrode surface, voltammograms were recorded at different scan rates ranging from 5 to 100 mV/s under the same analyte conditions, that is, the fixed 15 mM glucose concentration and a 0.1 M KOH solution. As the value of the scan rate increased, the peak potential shifted to a more positive zone which explains the diffusion limiting process at the electrode surface as has been shown in Figure 6c. With an increasing scan rate at a fixed concentration of analyte, the higher current values were obtained because of a fast electrolyte flux toward the electrode. Figure 6d shows a linear relationship between the square root of the scan rate and the current density up to a value of 60 mV/s scan rate and at higher values the current increment declined by the higher scan rate which showed the lower diffusion coefficient of the biomolecule. The value of slope further confirms that the process occurring at the electrode

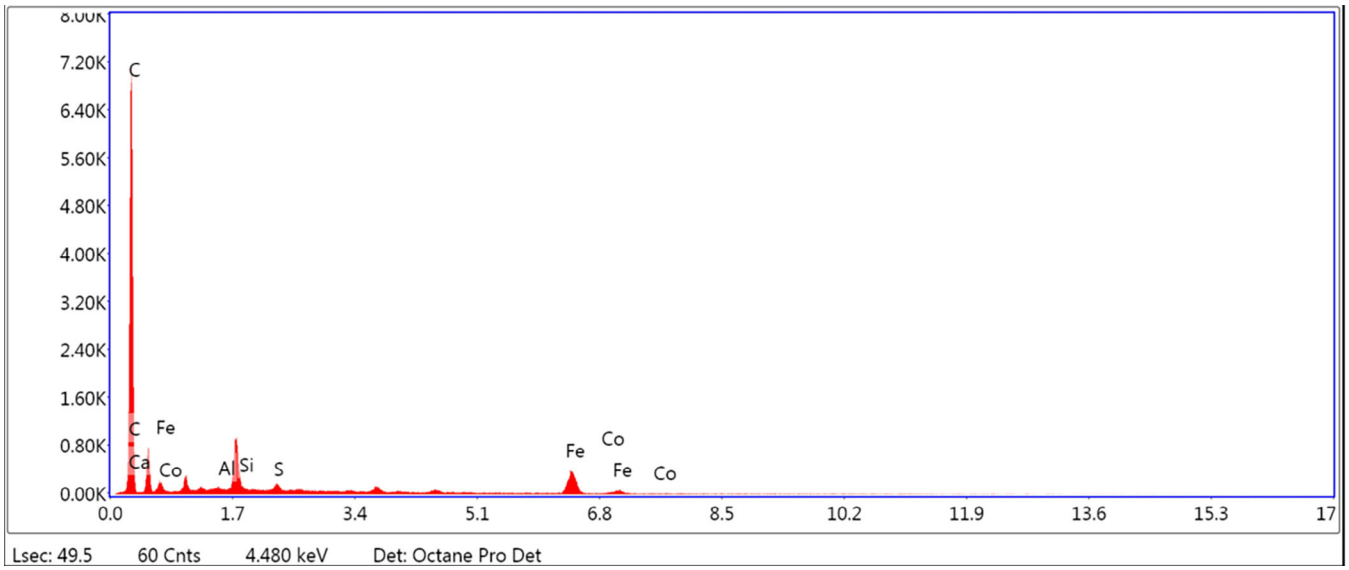

FIGURE 4 | Percentage ratio for the different elements in energy dispersive spectra.

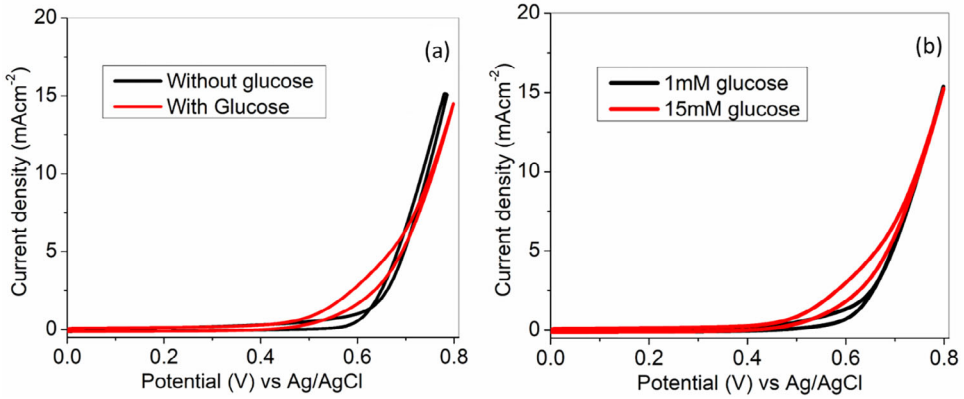

FIGURE 5 | Cyclic voltammograms (CVs) of $CoFe_2O_4$@CNTs fiber electrodes in 0.1 M potassium hydroxide (KOH) solution (a) with and without glucose at a fixed scan rate of 50 mV/s. (b) Cyclic voltammograms (CVs) of $CoFe_2O_4$@CNTs fiber electrode at 1st and 15th mM concentration.

surface is diffusion-controlled within the specific scan rate values.

The electrochemical behavior of the prepared catalyst, that is, $CoFe_2O_4$ toward glucose can be divided into three steps, which have been provided below in Equations (1)–(3).

$$CoFe_2O_4 + OH^- + H_2O \rightarrow CoOOH + 2FeOOH + e^- \quad (1)$$

$$CoOOH + OH^- \rightarrow CoO_2 + H_2O + e^- \quad (2)$$

$$FeOOH + CoO_2 + C_6H_{12}O_6 \rightarrow Fe(OH)_2 + CoOOH + C_6H_{10}O_6 \quad (3)$$

In the first step, CoF_2O_4 reacts with OH^- ion and produces FeOOH and CoOOH. In the second step, CoOOH reacts with OH^- ions to produce CoO_2. Finally, after the addition of glucose to an electrolyte solution containing 0.1 M KOH, FeOOH and CoO_2 catalyze glucose to glucolactone. These processes result in an irreversible glucose oxidation at the electrode surface.

3.3 | Amperometric Response

In order to explore the sensitivity of the modified electrode ($CoFe_2O_4$@CNTs fiber), its amperometric response was examined in 0.1 M KOH solution ($pH = 13$) with the addition of various glucose concentrations (1–15 mM) at a fixed potential of 0.6 V versus Ag/AgCl. To investigate the sensing parameters such as sensitivity and the limit of detection, chronoamperometry was carried out at constant potential with the addition of glucose for 30 sec. The electrochemical activity is highly dependent upon the concentration of OH^{-1} ion in a solution. To examine the influence of electrolyte concentration on the activity of the prepared electrode, an amperometric measurement was performed at 0.1 M KOH solution. As shown in Figure 7a, the electrode current density increased with an increase in the concentration of glucose until the glucose concentration increased beyond 15 mM. All the measurements were performed with constant stirring to ensure

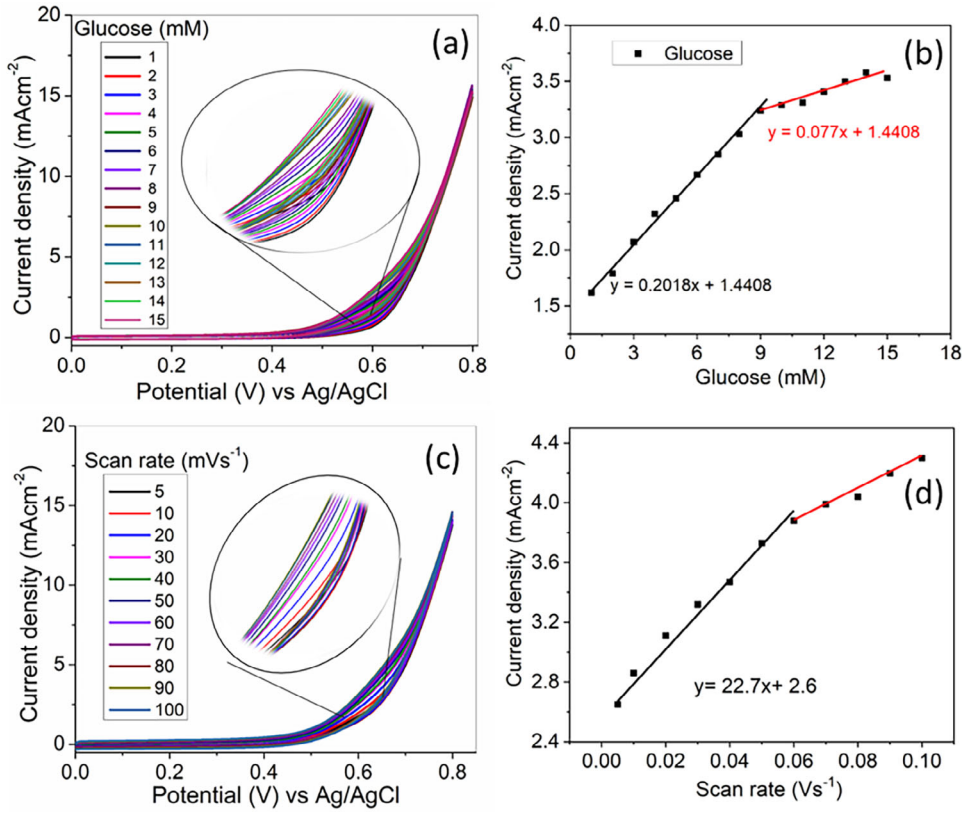

FIGURE 6 | (a) Cyclic voltammograms (CVs) of $CoFe_2O_4$@CNTs fiber in 0.1 M potassium hydroxide (KOH) with various concentrations of glucose (1–15 mM) at a scan rate of 50 mV/s. (b) The corresponding calibration plot of the anodic peak current with concentration. (c) Cyclic voltammograms (CVs) of $CoFe_2O_4$@CNTs fiber in 0.1 M KOH electrolyte containing 15 mM glucose with varied scan rate 5–100 mV/s. (d) The corresponding fitting plot of faradic currents versus square root of scan rate.

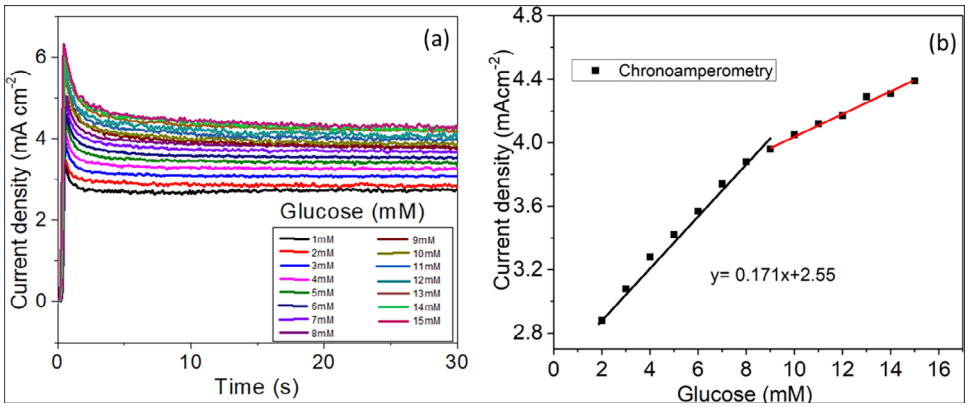

FIGURE 7 | (a) Amperometric response of $CoFe_2O_4$@CNTs fiber after the addition of various concentrations of glucose (1–15 mM) at 0.6 V and (b) its corresponding calibration curve, for current density versus concentration.

proper mixing of the analyte with electrolyte and ease of the flow of the analyte toward the electrode surface. A calibration straight line derived from current-time response exhibits a sensitivity of 0.17 μA mM^{-1} cm^{-2} with a linear range of 1–8 mM (see Figure 7b). The limit of detection (LOD) for the sensor was also calculated using the same calibration straight line with the help of standard deviation (σ) and slope (m), and it was found to be 1.9 mM. The electrochemical parameters for the fabricated sensors are almost compatible with both cyclic voltammetry and chronoamperometric studies.(Table 1)

3.4 | Electrochemical Impedance Spectroscopy

In order to examine the charge transfer resistance, EIS was conducted at a DC potential of 0.6 V in 0.1 M KOH solution containing 15 mM glucose. Charge transfer resistance of bare CNTs fiber and modified fiber could be quantified by semicircle in the Nyquist plot. The term charge transfer resistance (R_{ct}) is equal to the diameter of the semicircle which exhibits the electrochemical behavior of the electrode toward glucose oxidation. In the Nyquist plot (as shown in Figure 8), the Fe_2O_3@CNTs fiber

TABLE 1 | Comparison of Electrochemical performance of $CoFe_2O_4$@CNTs fiber with some other reported sensors in the literature.

Electrode material	Linear range (mM)	Sensitivity ($\mu A\ mM^{-1}\ cm^{-2}$)	LOD (μM)	Operation potential (V)	Medium	Refs.
$CoFe_2O_4$@N-CNFs	0.01–3.52	318	0.325	0.55	0.1 M NaOH	[31]
$CoFe_2O_4$ @MnO_2	—	1362.83	1.32	0.25	—	[32]
3-D/Ni–Fe@CFP	0.05–0.2	7.90	0.031	0.65	0.1 M NaOH	[33]
$CoNi_2S_4$@NCF	0.5–12.5	6.675	—	0.4	0.1 M NaOH	[34]
Ni(PDA)MOF@CNF	0.01–3	9457.5	0.053	0.55	0.1 M NaOH	[35]
CNF@ NiCo@GCE	0.001–2	1470	0.03	0.35	0.1 M NaOH	[26]
$CuCo_2O_4$@NiO	0.0005–6	4140	—	0.55	0.1 M NaOH	[27]
Cu-Sn@CP	2.0–10.0	—	—	0.55	—	[36]
GF@AuNS fiber	—	1045	1.15	0.2	0.1 M NaOH	[31]
CNT fibers	0.0015–0.098	0.308	0.38	0.23	3 M KCl 5mMFe(CN)6	[36]
LSCNO oxide nanofibers	0.1–1.0	924 ± 28	83	0.55	0.1 M NaOH	[36]
$Ni(OH)_2$@CNT fiber	0.02–10	12200	0.645	0.46	0.1 M NaOH	[34]
$CuCo_2O_4$@CNF	0.5–1.5	2932	0.15	0.25	0.1 M NaOH	[34]
NiFe@PANi	0.01–1	1050	0.5	0.50	0.1 M NaOH	[36]
CuO@CFF	0.96	6476.0	0.27	0.45	0.1 M NaOH	[37]
$CoFe_2O_4$@CNTs fiber	1–9	0.21	1.7 mM	0.56	0.1 M KOH	This work

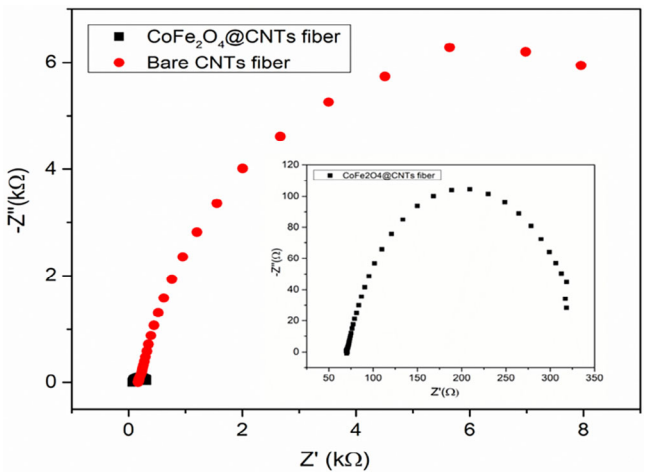

FIGURE 8 | Nyquist plots of bare and modified $CoFe_2O_4$@CNTs fiber in 0.1 M potassium hydroxide (KOH) solution containing 15 mM glucose with AC frequency at the range of 0.1 Hz–1 MHz at DC potential 0.6 V.

shows comparatively a smaller semicircle diameter in contrast to the bare CNTs fiber. Hence, the impedance result proved that the fabricated CNT fiber exhibits higher electrocatalytic activity and facilitates the charge transfer flow as compared to the bare CNT fiber [35].

4 | Conclusions

The $CoFe_2O_4$ nanoparticles have been prepared successfully via the facile hydrothermal method. The electrochemical measurements including cyclic voltammetry, chronoamperometry, and EIS were carried out in 0.1 M KOH for the detection of glucose. The prepared cobalt-iron oxide nanoparticles @CNTs fiber provide a good linear range of up to 9 mM glucose concentration with a sensitivity of 0.21 $\mu A\ mM^{-1}\ cm^{-2}$ and a low detection limit of 1.7 mM for the determination of glucose. The $CoFe_2O_4$ nanoparticles also provided pretty good selectivity and stability. Modified fiber (CNTs@$CoFe_2O_4$) showed the synergistic effect of the catalytic activity (provided by the $CoFe_2O_4$ nanoparticles) and the inner pathway (provided by the CNTs fiber) for glucose oxidation and charge transfer purposes. The fabricated electrode material appeared to have a promising potential to fabricate a flexible and wearable electrode for biosensing applications.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data are contained within the article.

References

1. M. Li, L. Fang, H. Zhou, et al., "Three-Dimensional Porous MXene/NiCo-LDH Composite for High Performance Non-Enzymatic Glucose Sensor," *Applied Surface Science* 495 (2019): 143554.

2. N. Chaianantakul, K. Wutthi, N. Kamput, et al., "Development of Mini-Spectrophotometer for Determination of Plasma Glucose," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 204 (2018): 670–676.

3. Z. Li, P. Huo, C. Gong, C. Deng, and S. Pu, "Boric-Acid-Modified Fe_3O_4@PDA@UiO-66 for Enrichment and Detection of Glucose by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry," *Analytical and Bioanalytical Chemistry* 412 (2020): 8083–8092.

4. J. Chen, J. Yan, B. Dou, Q. Feng, X. Miao, and P. Wang, "Aggregatable Thiol-Functionalized Carbon Dots-Based Fluorescence Strategy for Highly Sensitive Detection of Glucose Based on Target-Initiated Catalytic Oxidation," *Sensors and Actuators B: Chemical* 330 (2021): 129325.

5. C. Wei, X. Zou, Q. Liu, S. Li, C. Kang, and W. Xiang, "A Highly Sensitive Non-Enzymatic Glucose Sensor Based on CuS Nanosheets Modified Cu_2O/CuO Nanowire Arrays," *Electrochimica Acta* 334 (2020): 135630.

6. a) Dhanjai, X. Lu, L. Wu, J. Chen, and Y. Lu, "Robust Single-Molecule Enzyme Nanocapsules for Biosensing With Significantly Improved Biosensor Stability," *Analytical Chemistry* 92 (2020): 5830–5837. b) X. Zhou, X. Gu, Z. Chen, Y. Wu, W. Xu, and J. Bao, "A Novel and Sensitive Cu_2ZnSnS_4 Quantum Dot–Based Non–Enzymatic Glucose Sensor," *Sensors and Actuators B: Chemical* 329 (2021): 129117.

7. a) M. Wooten, S. Karra, M. Zhang, and W. Gorski, "On the Direct Electron Transfer, Sensing, and Enzyme Activity in the Glucose Oxidase/Carbon Nanotubes System," *Analytical Chemistry* 86 (2014): 752–757. b) Z. Zhang, Z. Tang, T. Su, W. Li, and Q. Wang, "Hydrogel-Coated Enzyme Electrodes Formed by GO_x-Mediated Polymerization for Glucose Detecting," *RSC Advances* 5 (2015): 47244–47247.

8. D. Jiang, Q. Liu, K. Wang, et al., "Enhanced Non-Enzymatic Glucose Sensing Based on Copper Nanoparticles Decorated Nitrogen-Doped Graphene," *Biosensors and Bioelectronics* 54 (2014): 273–278.

9. a) W. Li, H. Qi, B. Wang, et al., "Ultrathin $NiCo_2O_4$ Nanowalls Supported on a 3D Nanoporous Gold Coated Needle for Non-Enzymatic Amperometric Sensing of Glucose," *Microchimica Acta* 185 (2018): 1–9. b) T.-H. Ko, S. Radhakrishnan, M.-K. Seo, M.-S. Khil, H.-Y. Kim, and B.-S. Kim, "A Green and Scalable Dry Synthesis of $NiCo_2O_4$/Graphene Nanohybrids for High-Performance Supercapacitor and Enzymeless Glucose Biosensor Applications," *Journal of Alloys and Compounds* 696 (2017): 193–200. c) K. K. Naik, S. Sahoo, and C. S. Rout, "Facile Electrochemical Growth of Spinel Copper Cobaltite Nanosheets for Non-Enzymatic Glucose Sensing and Supercapacitor Applications," *Microporous and Mesoporous Materials* 244 (2017): 226–234.

10. a) C. H. Chou, J. C. Chen, C. C. Tai, I. W. Sun, and J. M. Zen, "A Nonenzymatic Glucose Sensor Using Nanoporous Platinum Electrodes Prepared by Electrochemical Alloying/Dealloying in a Water-Insensitive Zinc Chloride-1-Ethyl-3-Methylimidazolium Chloride Ionic Liquid," *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis* 20 (2008): 771–775. b) Y. Ding, Y. Wang, L. Su, M. Bellagamba, H. Zhang, and Y. Lei, "Electrospun Co_3O_4 Nanofibers for Sensitive and Selective Glucose Detection," *Biosensors and Bioelectronics* 26 (2010): 542–548. c) R. A. Soomro, Z. H. Ibupoto, M. I. Abro, and M. Willander, "Electrochemical Sensing of Glucose Based on Novel Hedgehog-Like NiO Nanostructures," *Sensors and Actuators B: Chemical* 209 (2015): 966–974. d) X. Tang, B. Zhang, C. Xiao, H. Zhou, X. Wang, and D. He, "Carbon Nanotube Template Synthesis of Hierarchical $NiCo_2O_4$ Composite for Non-Enzyme Glucose Detection," *Sensors and Actuators B: Chemical* 222 (2016): 232–239.

11. a) X. Xu, B. Dong, S. Ding, C. Xiao, and D. Yu, "Hierarchical $NiCo_2O_4$ Nanosheets Supported on Amorphous Carbon Nanotubes for High-Capacity Lithium-Ion Batteries With a Long Cycle Life," *Journal of Materials Chemistry A* 2 (2014): 13069–13074. b) R. Wu, X. Qian, K. Zhou, J. Wei, J. Lou, and P. M. Ajayan, "Porous Spinel $Zn_xCo_{3-x}O_4$ Hollow Polyhedra Templated for High-Rate Lithium-Ion Batteries," *ACS Nano* 8 (2014): 6297–6303.

12. a) X. Xu, H. Zhou, S. Ding, J. Li, B. Li, and D. Yu, "The Facile Synthesis of Hierarchical $NiCo_2O_4$ Nanotubes Comprised Ultrathin Nanosheets for Supercapacitors," *Journal of Power Sources* 267 (2014): 641–647. b) D. Cai, B. Liu, D. Wang, et al., "Construction of Unique $NiCo_2O_4$ Nanowire@$CoMoO_4$ Nanoplate Core/Shell Arrays on Ni Foam for High Areal Capacitance Supercapacitors," *Journal of Materials Chemistry A* 2 (2014): 4954–4960. c) S. Peng, L. Li, H. B. Wu, S. Madhavi, and X. W. Lou, "Controlled Growth of $NiMoO_4$ Nanosheet and Nanorod Arrays on Various Conductive Substrates as Advanced Electrodes for Asymmetric Supercapacitors," *Advanced Energy Materials* 5 (2015): 1401172.

13. a) M. H. Habibi and J. Parhizkar, "Cobalt Ferrite Nano-Composite Coated on Glass by Doctor Blade Method for Photo-Catalytic Degradation of an Azo Textile Dye Reactive Red 4: XRD, FESEM and DRS Investigations," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 150 (2015): 879–885. b) S. M. Alshehri, A. N. Alhabarah, J. Ahmed, M. Naushad, and T. Ahamad, "An Efficient and Cost-Effective Tri-Functional Electrocatalyst Based on Cobalt Ferrite Embedded Nitrogen Doped Carbon," *Journal of Colloid and Interface Science* 514 (2018): 1–9.

14. a) Q. Zafar, M. I. Azmer, A. G. Al-Sehemi, M. S. Al-Assiri, A. Kalam, and K. Sulaiman, "Evaluation of Humidity Sensing Properties of TMBH-PET Thin Film Embedded With Spinel Cobalt Ferrite Nanoparticles," *Journal of Nanoparticle Research* 18 (2016): 1–12. b) J. Paulsen, A. Ring, C. Lo, J. E. Snyder, and D. C. Jiles, "Manganese-Substituted Cobalt Ferrite Magnetostrictive Materials for Magnetic Stress Sensor Applications," *Journal of Applied Physics* 97 (2005): 044502.

15. D.-H. Kim, D. E. Nikles, D. T. Johnson, and C. S. Brazel, "Heat Generation of Aqueously Dispersed $CoFe_2O_4$ Nanoparticles as Heating Agents for Magnetically Activated Drug Delivery and Hyperthermia," *Journal of Magnetism and Magnetic Materials* 320 (2008): 2390–2396.

16. M. P. Pileni, "Magnetic Fluids: Fabrication, Magnetic Properties, and Organization of Nanocrystals," *Advanced Functional Materials* 11 (2001): 323–336.

17. D. Erdem, N. S. Bingham, F. J. Heiligtag, et al., "$CoFe_2O_4$ and $CoFe_2O_4$-SiO_2 Nanoparticle Thin Films With Perpendicular Magnetic Anisotropy for Magnetic and Magneto-Optical Applications," *Advanced Functional Materials* 26 (2016): 1954–1963.

18. S. M. Alshehri, J. Ahmed, A. N. Alhabarah, T. Ahamad, and T. Ahmad, "Nitrogen-Doped Cobalt Ferrite/Carbon Nanocomposites for Supercapacitor Applications," *ChemElectroChem* 4 (2017): 2952–2958.

19. A. Samavati and A. Ismail, "Antibacterial Properties of Copper-Substituted Cobalt Ferrite Nanoparticles Synthesized by co-Precipitation Method," *Particuology* 30 (2017): 158–163.

20. W. Chen, C. Xia, and N. Husam, "One-Step Electrodeposited Nickel Cobalt Sulfide Nanosheet Arrays for High-Performance Asymmetric Supercapacitors," *American Chemical Society Nano* 8 (2014): 9531–9541.

21. B. Fall, D. D. Sall, M. Hémadi, et al., "Highly Efficient Non-Enzymatic Electrochemical Glucose Sensor Based on Carbon Nanotubes Functionalized by Molybdenum Disulfide and Decorated With Nickel Nanoparticles (GCE/CNT/MoS_2/NiNPs)," *Sensors and Actuators Reports* 5 (2023): 100136.

22. B. A. Hussein, A. A. Tsegaye, G. Shifera, and A. M. Taddesse, "A Sensitive Non-Enzymatic Electrochemical Glucose Sensor Based on a ZnO/Co_3O_4/Reduced Graphene Oxide Nanocomposite," *Sensors and Diagnostics* 2 (2023): 347–360.

23. M. Mathew, S. Radhakrishnan, A. Vaidyanathan, B. Chakraborty, and C. S. Rout, "Flexible and Wearable Electrochemical Biosensors Based on Two-Dimensional Materials: Recent Developments," *Analytical and Bioanalytical Chemistry* 413 (2021): 727–762.

24. S. Dong, H. Niu, L. Sun, et al., "Highly Dense Ni-MOF Nanoflake Arrays Supported on Conductive Graphene/Carbon Fiber Substrate as

Flexible Microelectrode for Electrochemical Sensing of Glucose," *Journal of Electroanalytical Chemistry* 911 (2022): 116219.

25. M. Elancheziyan, K. Prakasham, M. Eswaran, et al., "Eco-Friendly Fabrication of Nonenzymatic Electrochemical Sensor Based on Cobalt/Polymelamine/Nitrogen-Doped Graphitic-Porous Carbon Nanohybrid Material for Glucose Monitoring in human Blood," *Environmental Research* 223 (2023): 115403.

26. S. Lee, J.-G. Kim, H. Yu, et al., "Flexible Supercapacitor With Superior Length and Volumetric Capacitance Enabled by a Single Strand of Ultra-Thick Carbon Nanotube Fiber," *Chemical Engineering Journal* 453 (2023): 139974.

27. Á. Torrinha and S. Morais, "Electrochemical (bio)Sensors Based on Carbon Cloth and Carbon Paper: An Overview," *TrAC Trends in Analytical Chemistry* 142 (2021): 116324.

28. M. Mathew, S. Radhakrishnan, A. Vaidyanathan, B. Chakraborty, and C. S. Rout, "Flexible and Wearable Electrochemical Biosensors Based on Two-Dimensional Materials: Recent Developments," *Analytical and Bioanalytical Chemistry* 413 (2021): 727–762.

29. A. Nazir, S. Muqaddas, A. Ali, et al., "A Flexible Carbon Nanotubes-Based Microelectrode for Non-Enzymatic Electrochemical Uric Acid and Ascorbic Acid Sensing," *Materials Science and Engineering: B* 307 (2024): 117480.

30. A. Ali, S. Muqaddas, H. Aldosari, et al., "Novel Structured Carbon Nanotubes fiber Based Microelectrodes for Efficient Electrochemical Water Splitting and Glucose Sensing," *Carbon* 218 (2024): 118709.

31. Y. Ding, C. Ren, X. Tian, et al., "Facile Synthesis of Aminophenylboronic Decorated Electrospun $CoFe_2O_4$ Spinel Nanofibers With Enhanced Electrocatalytic Performance for Glucose Electrochemical Sensor Application," *Ceramics International* 47 (2021): 19052–19062.

32. G. He, Y. Wen, C. Ma, L. Wang, L. Gao, and Z. Sun, "Detection of Glucose Using a Thin-Walled Honeycombed MnO_2 Grown on Mesoporous $CoFe_2O_4$ Nanosheets," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 660 (2023): 130817.

33. P. Kannan, T. Maiyalagan, E. Marsili, S. Ghosh, J. Niedziolka-Jönsson, and M. Jönsson-Niedziolka, "Hierarchical 3-Dimensional Nickel–iron Nanosheet Arrays on Carbon fiber Paper as a Novel Electrode for Non-Enzymatic Glucose Sensing," *Nanoscale* 8 (2016): 843–855.

34. M. Dong, H. Hu, S. Ding, C. Wang, and L. Li, "Flexible Non-Enzymatic Glucose Biosensor Based on $CoNi_2S_4$ Nanosheets Grown on Nitrogen-Doped Carbon Foam Substrate," *Journal of Alloys and Compounds* 883 (2021): 160830.

35. B. Dey, M. W. Ahmad, G. Sarkhel, D.-J. Yang, and A. Choudhury, "Fabrication of Porous Nickel (II)-Based MOF@Carbon Nanofiber Hybrid Mat for High-Performance Non-Enzymatic Glucose Sensing," *Materials Science in Semiconductor Processing* 142 (2022): 106500.

36. K. D. Pelucarte, T. A. Hatchell, G. George, et al., "Electrospun Porous La–Sr–Co–Ni–O Nanofibers for Highly Sensitive Non-Enzymatic Glucose Detection," *Materials Advances* 3 (2022): 2096–2103.

37. X. Wang, E. Liu, and X. Zhang, "Non-Enzymatic Glucose Biosensor Based on Copper Oxide-Reduced Graphene Oxide Nanocomposites Synthesized From Water-Isopropanol Solution," *Electrochimica Acta* 130 (2014): 253–260.