Non-Enzymatic Glucose Sensor Based on Ni(OH)₂/NF Materials Using Different Pulse Voltammetry Technique

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Abstract

Non-enzymatic glucose sensors have gained significant attention owing to their potential for accurate and cost-effective glucose detection. Nanomaterials play a pivotal role in enhancing performance of non-enzymatic glucose sensor. In this study, a novel non-enzymatic glucose sensor based on Ni(OH)₂/NF (nickel hydroxide/nickel foam) materials was developed using different pulse voltammetry technique. Chemical precipitation methods have been used to grow Ni(OH)₂ nanostructures directly on a nickel foam electrode. The characterization of the synthesized materials was performed through field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDX), and X-ray diffraction (XRD). The performance of the Ni(OH)₂/NF-based glucose sensor was evaluated through electrochemical measurements. Nanoscale hive-like structures of Ni(OH)₂ with a diameter ranging from 450 to 530 µm and a thickness of 20 nm were formed on the NF surface. The sensor exhibited good performance, displaying a high sensitivity of 8.42mA.mM^{-1}.cm^{-2} with a low detection limit of 0.84 µM. These results position the synthesized electrode as a promising contender for non-enzymatic electrochemical glucose sensors.

Keywords: Ni(OH)₂ nanostructures, Ni foam, non-enzymatic glucose sensing, electrochemical sensor, direct growth.

1. Introduction

Glucose serves as the primary molecular marker for diabetes monitoring and variations in its concentration hold paramount importance for human well-being. The precise quantification of glucose carries profound implications not only for proactive healthcare management but also extends its significance to future applications in preventive medicine, ensuring food safety, environmental surveillance, pharmaceutical analysis, and advancements in biotechnology [1]. Electrochemical analysis has gained recognition as a highly efficient and accurately calibrated technique for glucose detection. Currently, electrochemical glucose sensors can be categorized into two main types: non-enzyme sensors and enzyme sensors, based on the catalysts utilized in the detection process [2].

In recent years, electrochemical non-enzyme sensors have gained considerable prominence in the realm of glucose detection due to their cost-effectiveness, exceptional efficiency, resilience against environmental fluctuation, and straightforward manufacturing processes [3]. A critical determinant for the performance of an exceptional electrochemical non-enzyme glucose sensor lies in the quality of its electro-catalysts, which should processes enduring stability, heightened sensitivity, and perfect selectivity. Non-enzymatic sensors exhibit noteworthy attributes such as heightened sensitivity, prolonged stability, rapid response times, and economical production [4]. Consequently, they have garnered escalating interest as compelling alternatives for surmounting the limitation inherent in enzymatic biosensors.

Many research groups have focused on the development of non-enzymatic sensors based on electrocatalytic oxidation of glucose on pure metal surfaces. Early investigations indicated that the oxidation of glucose on some noble metals, such as Pt and Au, behaved a sluggish kinetics and produced small faradaic currents [5]. In addition, noble metal surfaces proved susceptible to poisoning by adsorbed

intermediates and chloride ions, resulting in decreased sensitivity. Consequently, studying novel materials with suitable features has emerged as a pivotal factor in the construction of highly sensitive non-enzymatic glucose sensors.

In response to this challenge, numerous transition metal oxides or metal hydroxides, such as NiO, CuO, Co_3O_4 [6, 7], and $Ni(OH)_2$, [8, 9] have emerged as promising materials. Among these cost-effective candidates, nanostructures of $Ni(OH)_2$, a significant transition metal hydroxide, hold great promise as active electrode materials in non-enzymatic glucose electrochemical sensors [10]. $Ni(OH)_2$ materials can be fabricated via solgel synthesis [9], hydrothermal, and solvothermal methods [8] and then deposited on the electrode surface using a binder. Using a binder may increase electrode mass, modify electrode surface, or decrease charge transfer. To avoid using the binder, a simple method to grow $Ni(OH)_2$ directly on the electrode surface is in high demand. Direct growth of nanomaterials on the electrode surface offers several advantages, including enhanced materials-electrode bonding, fast charge transfer rate, and preservation of electrode surface.

In this paper, we reported a simple chemical precipitation method for the direct synthesis of nanostructured $Ni(OH)_2$ on nickel foam (NF). Nickel foam (NF) serves as an economical and versatile substrate characterized by its exceptional 3D porous architecture. This structure affords a substantial specific surface area, facilitating the deposition of nickel hydroxide and creating an abundance of sites crucial for the catalytic glucose reaction. Consequently, this configuration enhances the sensitivity of glucose detection, rendering nickel foam a promising substrate for glucose sensors. Furthermore, this method offers simplicity, cost-effectiveness, and the unique advantage of direct growth on electrode bases such as nickel foam. It is an environmentally friendly approach that can be easily implemented on a large scale, making it highly applicable across various fields.

2. Materials and Methods

2.1. Materials

All the chemical reagents employed in the experiment were of analytical grade, boasting a purity of 99.9%. Nickel(II) nitrate hexahydrate $(Ni[NO_3]_2.6H_2O)$ and D(+)-glucose were produced from Merck KgaA (64271 Darmstadt, Germany). Hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) was supplied by Tianjin Dengfeng Chemical Co., Ltd. Acetone (Xilong, China) and deionized water (DI) were also utilized in the experiments.

2.2. Synthesis of Ni(OH)₂ Nanostructure

The experimental procedure of $Ni(OH)_2$/NF electrode fabrication is shown in Fig. 1.
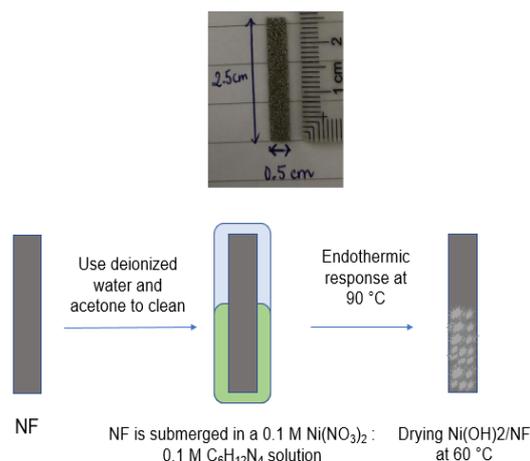

Fig. 1. Experiment procedure for fabrication of $Ni(OH)_2$/NF.

The substrate for the direct growth of $Ni(OH)_2$ nanostructures in this study was nickel foam (NF) with dimensions of 25 mm x 5 mm x 1.5 mm. The NF was cleaned in an ultrasonic bath containing acetone for 15 minutes, followed by another 15 minutes of immersion in deionized water. Subsequently, it was allowed to air dry for 30 minutes. In the next step, the cleaned NF was dipped in a solution composed 500ml of $C_6H_{12}N_4$ (HMTA) 0.5M and 500 ml of $Ni(NO_3)_2$ 0.5M. The synthesis of $Ni(OH)_2$ can be described through the following reactions:

$$C_6H_{12}N_4 + 6\ H_2O \leftrightarrow 6CH_2O + 4NH_3$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$$
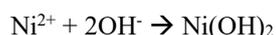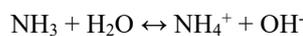
The mixture was then heated in an oven at 90 °C for different times (10, 30, and 50 minutes). After the heating process, the fabricated structures were rinsed thoroughly using deionized water to remove any residual substances. Finally, the sensor was dried at 60 °C before being ready for measurement.

The morphological attributes and elemental composition of the constructed materials were assessed through the utilization of field-emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDX), and X-ray diffraction (XRD).

2.3. Electrochemical Properties of Ni(OH)₂ and Glucose Measurement

All electrochemical measurements were ferformed in NaOH solution at ambient room temperature, employing three electrode system: Ag/AgCl as reference electrode, Pt wire as counter electrode, and $Ni(OH)_2$/NF as working electrode. Electrochemical properties of the fabricated $Ni(OH)_2$/NF electrode were characterized using cyclic voltammetry (CV) technique. The determination of

glucose concentrations was effectuated using differential pulse voltammetry (DPV).

3. Results and Discussion

3.1. Morphologies of the Ni(OH)₂/NF Materials

Fig. 2 delineates the FESEM images of the NF electrode and the synthesized $Ni(OH)_2$ nanostructures with various synthesized durations, corresponding to the samples of $Ni(OH)_2$ - 10m, $Ni(OH)_2$ - 30m, and $Ni(OH)_2$ - 50m. As shown in Fig 2a, no nanostructures were observed on the flat surface of the NF electrode. In contrast, following the formation of $Ni(OH)_2$, the substrate was covered with nanoscale hive-like structures (Fig. 2b-d). The samples manifest relatively uniform morphological features. The average diameter of pores on the electrode surface increases from 450 nm to 530 nm as synthesis time increases from 10 to 30min. This observed phenomenon is likely attributable to the progressive evolution of funnel-shaped pore structures over temporal progression. The thickness of the pore walls was estimated to be about 20 nm. The growth of nanohive structures of $Ni(OH)_2$ with very thin walls on NF electrode is favorable for the sensor, especially for an electrochemical sensor thanks to maximum adsorption ability. In addition, the direct growth of nanostructures on the electrode surface allows to avoid using extra binder, high temperature, or extra conductor.

3.2. Composition of the Ni(OH)₂/NF Materials

In order to analyse the composition of the synthesized materials, EDX technique was used. As shown in Fig. 3, $Ni(OH)_2$/NF samples primarily comprised of O (60.21%), C (28.36%), and Ni (11.42%). .The presence of C can be attributed to Hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) remaining in the sample, potential contamination from hydrocarbon compounds prevalent within the laboratory environment or arising from surface adsorption. Meanwhile, constituents' Ni and O are attributed to the $Ni(OH)_2$ sample. The prominent peaks of Ni, O, and C elements are clearly visible in the EDX spectrum, confirming the presence of $Ni(OH)_2$ structures atop the NF.

To ascertain the crystal structure of the electrode as it was manufactured, an XRD measurement was performed. The XRD patterns of $Ni(OH)_2$/NF are shown in Fig. 4. The characteristic peaks located at 45°, 52,7°, and 77° can be assigned to the (111), (200), (220) crystallographic planes of face-centered-cubic Ni crystal structure, respectively, (JCPDS 04-850).
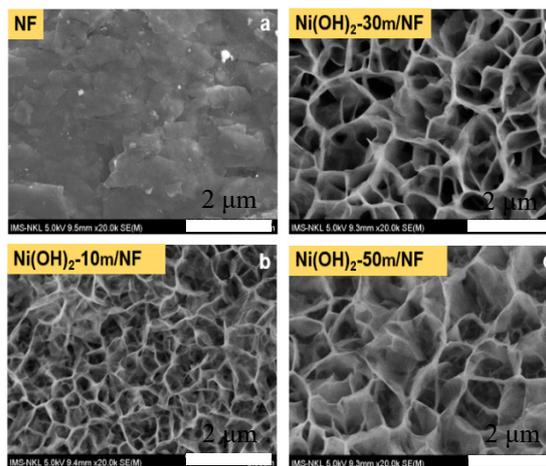

Fig. 2. FE-SEM images of (a) the bare NF and (b-d) the Ni(OH)₂/NF electrodes.
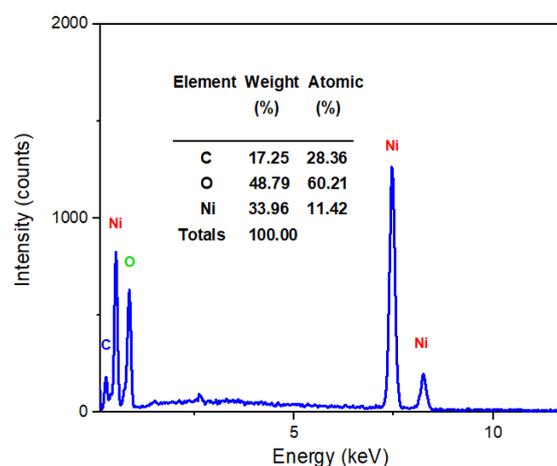

Fig. 3. EDX spectrum of Ni(OH)₂/NF.
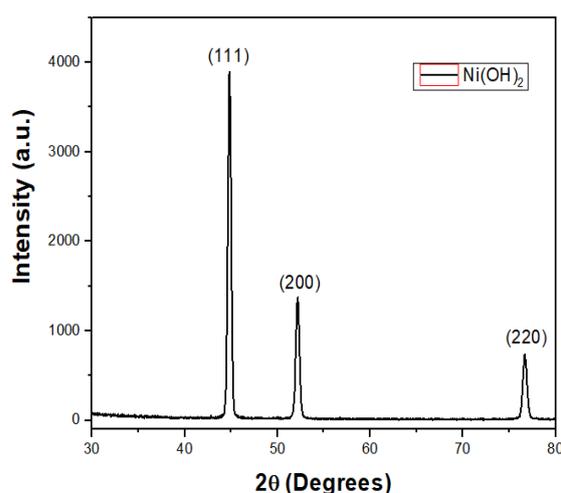
Fig. 4. X-ray diffraction patterns of Ni(OH)₂/NF films on Ni foam substrates.

3.3 Cyclic Voltammetry Measurement of the Synthesized Materials in Alkaline Medium

Fig. 5a, 5b, and 5c show the CV curves of the as-prepared $Ni(OH)_2/NF$-10m, $Ni(OH)_2/NF$-30m and $Ni(OH)_2/NF$-50m electrodes, respectively, in a potential range from -1.2 V to 1.6 V at a scan rate of 10 mV/s in a 0.1M NaOH solution. As shown in Fig. 5, anodic and cathodic peaks at potentials of 0.55 V and 0.2 V, respectively, representing the oxidation and reduction of the redox couple Ni^{2+}/Ni^{3+}, were observed.

In order to assess the reproducibility of electrodes, four distinct $Ni(OH)_2/NF$ electrodes that were fabricated under identical conditions were evaluated. The obtained results, as depicted in Fig. 5a, 5b, 5c, indicate that the variances observed in the cyclic voltammetry (CV) curves among the four sensors are minimal and insignificant. These results indicate that the fabricated $Ni(OH)_2/NF$ electrodes are stable for glucose measurement.
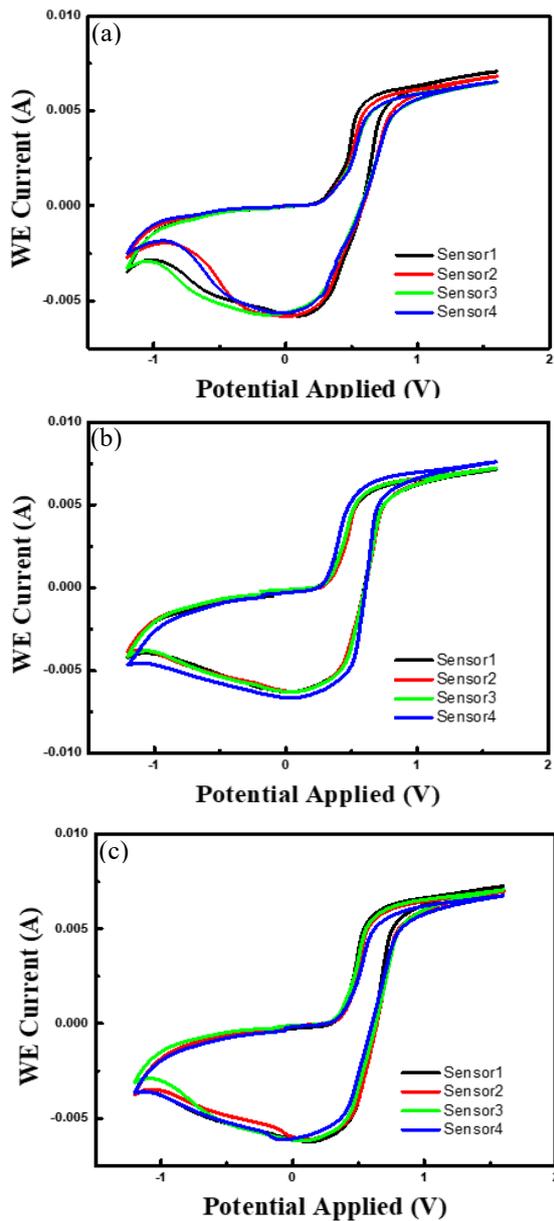
Fig. 5. CV curves of the a) $Ni(OH)_2/NF$-10m, b)$Ni(OH)_2/NF$-30m, c) $Ni(OH)_2/NF$-50m electrodes at a scan rate of 10 mV/s in 0.1 M NaOH.
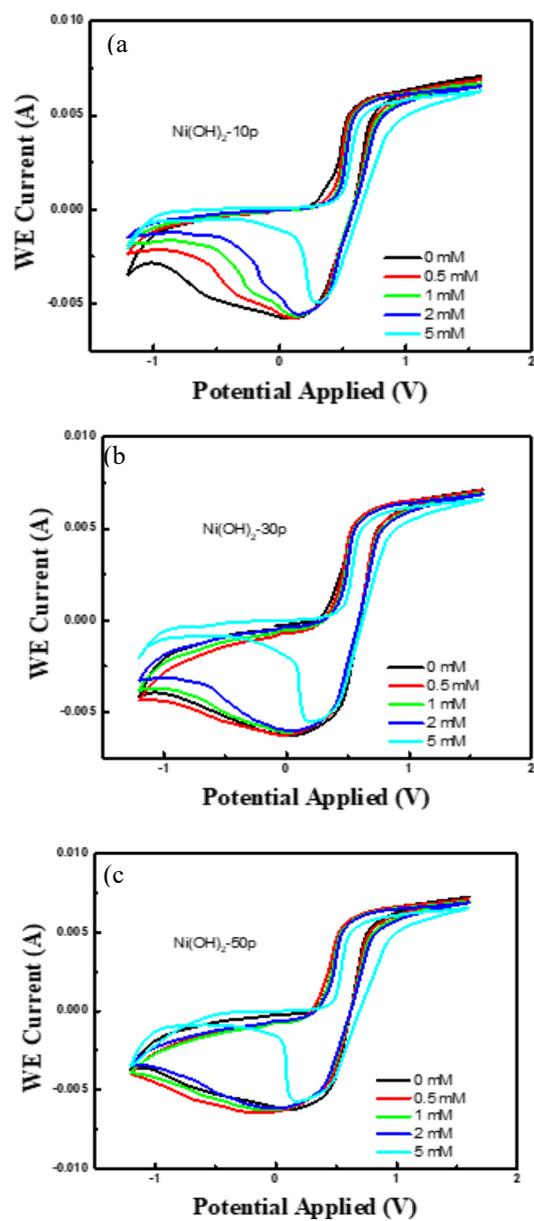

Fig. 6. CVs curves of (a) $Ni(OH)_2/NF$-10m, (b)$Ni(OH)_2/NF$-30m, (c) $Ni(OH)_2/NF$-50m electrodes in 20 mL NaOH 0.1M with glucose concentration from 0 to 5 mM.

3.4. Glucose Measurement

In order to test the sensitivity of the $Ni(OH)_2$/NF electrode to glucose, the cyclic voltammetry method was used. Fig. 6 presents the CV curves with different concentrations of glucose from 0 to 5 mM of three electrodes: $Ni(OH)_2$/NF-10m, $Ni(OH)_2$/NF-30m, and $Ni(OH)_2$/NF-50m in 0.1M NaOH solution at a scan rate of 10 mV/s.

The findings illustrated in Fig. 6a reveal that as the glucose concentration increases from 0 to 5 mM, there is a gradual reduction observed in both the cathodic and anodic peak currents. Notably, the response of the cathodic and anodic peaks remains relatively unchanged when glucose concentrations oscillate within the range of 0 to 2 mM for the $Ni(OH)_2$/NF-30m and $Ni(OH)_2$/NF-50m electrodes (Fig. 6b,c). It is only at the glucose concentration of 5 mM that discernible alterations in the cathodic and anodic peaks become apparent. Evidently, the $Ni(OH)_2$/NF-10m electrode demonstrates enhanced responsiveness to glucose, particularly at lower concentrations below 2 mM. The $Ni(OH)_2$/NF-10m electrode was chosen for further examination.

To further investigate the electrocatalytic activity of $Ni(OH)_2$/NF-10m for glucose oxidation, the DPV technique was used. DPV measurements were conducted to detect glucose with a concentration range from 0 to 5 mM in 0.1 M NaOH. Fig. 7a distinctly illustrates the progressive diminution in peak current as the glucose concentration escalates from 0 to 5 mM. The relationship between the response current and glucose concentration is expounded further within the calibration plot, as shown in Fig. 7b. The observed data indicates a consistent reduction in current as the concentration of glucose increases. This relationship can be mathematically represented by the following equation, which describes a linear decrease:

$$I\ (mA) = 0.00115 - 5.47224 * C_G \tag{1}$$

where C_G represents glucose concentration, measured in mM. The coefficient of determination, often denoted R^2, is approximately 0.9918. The sensitivity, determined by dividing the slope by the working electrode area (0.65 cm^2), is 8.42 $mA.mM^{-1}.cm^{-2}$). The detection limit, as established using a signal-to-noise ratio of three, is 0.84 μM [11]. The produced $Ni(OH)_2$/NF electrodes, exhibiting elevated sensitivity, rapid responsibility, and low limit of detection, are assessed as promising candidates for practical applications.

A comparison of our findings with recent publications concerning glucose sensors employing nickel foam substrates or $Ni(OH)_2$ materials is presented in Table 1. Among the published nickel-based non-enzymatic glucose sensors, the electrode featuring ultrathin walls, measuring approximately 20 nm, composed of $Ni(OH)_2$ nanohives atop a remarkably conductive nickel foam substrate stands out as a prime example of heightened sensitivity. This elevation in sensitivity is attributed to the augmented surface area conferred by the porosity intrinsic of $Ni(OH)_2$ nanohives. Notably, in relation to the linear range of glucose quantification, our finding is quite extensive, measuring from 0.05 to 5 mM. The results indicate that the $Ni(OH)_2$/NF electrode is capable of detecting glucose in an alkaline solution.


(a)

(b)
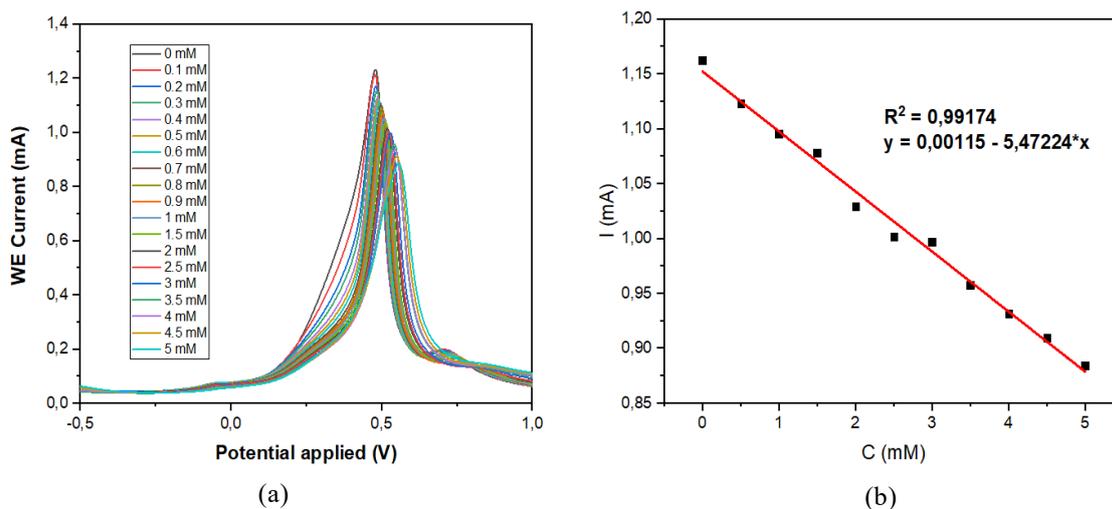
Fig. 7. a) DPV curve of $Ni(OH)_2$/NF-10m working electrode in 0.1 M NaOH containing glucose with the concentration range from 0 mM to 5 mM at a scan rate of 50 mV/s vs. Ag/AgCl and b) the calibration plot of response current vs. glucose concentration.

Table 1. Performance comparison of various glucose sensors

Materials	Sensitivity ($mA\ mM^{-1}\ cm^{-2}$)	Limit of detection (μM)	Linear range (mM)	Ref
$NiCo_2O_4$@Ppy/NF	3.06	0.22	0.001-20	[10]
$Ni(OH)_2$ nanowires/NF	1.60	1	0.1-6	[12]
$Ni(OH)_2$ nanosheet/Ni	1.13	1	0.002-0.04	[13]
$Ni(OH)_2$ NPs/NF	1.95	0.16	0-6	[14]
$Ni(OH)_2$/PGE	0.948	2	0.004-3.5	[15]
$Ni(OH)_2$/TiO_2	0.192	8	0.03-14	[16]
$Ni(OH)_2$/NF	8.42	0.84	0.05-5	This work

6. Conclusion

A simple and cost-effective chemical process was employed to successfully synthesize $Ni(OH)_2$ porous nanostructures directly on the surface of a nickel foam substrate. These fabricated electrodes were then utilized to measure glucose concentration in an alkaline medium at room temperature using CV and DPV methods. The non-enzymatic glucose sensors based on the $Ni(OH)_2$-coated nickel foam demonstrated excellent performance characteristics. They exhibited remarkable repeatability, high sensitivity ($8.42\ mA.mM^{-1}.cm^{-2}$), and a low limit of detection ($0.84\ \mu M$). These outcomes underscore the substantial promise of the synthesized $Ni(OH)_2$-coated nickel foam electrodes for application in non-enzymatic glucose electrochemical sensors, particularly in clinical medical settings.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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