Nonenzymatic Glucose Sensor Based on Porous Co₃O₄ Nanoneedles

Jianchun Sun,¹ Hongjing Zhao,² and Zhongchang Wang¹,3

¹College of Metallurgy and Materials Engineering, Chongqing University of Science and Technology, Chongqing 401331, China
²Chongqing Ecological Environment Monitoring Center, Chongqing 400030, China
³International Iberian Nanotechnology Laboratory, Braga 4715-330, Portugal

Correspondence should be addressed to Jianchun Sun; jianchunsun@cqust.edu.cn and Hongjing Zhao; zjzhj@163.com

Received 20 July 2022; Accepted 14 September 2022; Published 8 October 2022

Copyright © 2022 Jianchun Sun et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Herein, porous Co₃O₄ nanoneedle arrays were synthesized on nickel (Ni) foam (Co₃O₄ NNs/NF) by one-step hydrothermal method. Some electrochemical methods were used to investigate its nonenzymatic glucose sensing performance in alkaline solution. The results show that the sensitivity of Co₃O₄ NNs/NF electrode to glucose is 4570 μA M⁻¹ cm⁻². The linear range is 1 μM - 0.337 mM, and the detection limit is 0.91 μM (S/N = 3). It also displays good selectivity and repeatability for glucose. The good electrochemical sensing performance of Co₃O₄ NNs/NF based sensor for glucose can be attributed to interconnected porous structure and large specific surface area of Co₃O₄.

1. Introduction

Rapid and accurate detection of blood glucose concentration is very important for the diagnosis and treatment of diabetes. Although graphene oxide based glucose sensor dominates the market, it has some defects, such as high cost, limited stability, and complex enzyme immobilization process [1, 2]. In recent years, nonenzymatic glucose sensors have attracted the attention of a large number of researchers because of their advantages such as low cost, good stability, fast response, and simple fabrication [3].

Electrocatalytic active materials modified on the electrode surface have a great impact on the performance of nonenzymatic glucose sensor [4]. So far, a series of nanstructured materials based on precious metals and their alloys (such as Pt, Ag, Pd, Au, Pt-Pd, and Pt-Au) have excellent electrochemical catalytic oxidation activity, which has been proved to be used for the electrocatalytic oxidation of glucose [5–8]. However, due to the scarcity and high cost of these precious metals, the surface of precious metal based materials is usually easily polluted by adsorbed intermediates and chloride ions, which greatly affects the stability and sensitivity of the sensor [9, 10]. In view of this, researchers try to develop electrode materials with high performance and low cost for nonenzymatic glucose sensing. In particular, transition metal oxides have the advantages of low price and high conductivity. They are regarded as the ideal electrode active materials for nonenzymatic glucose sensing [11, 12]. Among them, Co₃O₄ is an ionic semiconductor with both polar positive electrodes (two Co²⁺, two Co³⁺, and four O²⁻) and polar negative electrodes (two Co⁷⁺ and four O²⁻). It has excellent electrochemical performance and has been widely used in photocatalysis, supercapacitors, lithium-ion batteries, electrochemical sensors, and other fields [13]. Therefore, Co₃O₄, which has good lasting stability and electrocatalytic activity in alkaline medium, is also one of the most promising materials for electrocatalytic oxidation of glucose.

As we all know, different morphologies and microstructures of materials would produce substantial differences in their surface area, particle size, pore structure, mass transfer, and electron transfer efficiency, which will affect their electrochemical sensing performance [14]. Therefore, construction of Co₃O₄ with excellent microstructure can effectively enhance the electrocatalytic performance of glucose. If the Co₃O₄ catalytic material is directly grown on the conductive substrate in the form of well-arranged nanoarrays, the
performance of the catalytic material can be effectively improved. In this work, one-step hydrothermal method was used to prepare porous Co$_3$O$_4$ nanoneedle arrays (Co$_3$O$_4$ NNs/NF) in situ on Ni foam. With the help of the three electrode system, the electrochemical performance of the self-supporting electrode in situ was tested. The results show that Co$_3$O$_4$ NNs/NF exhibits higher sensitivity, lower detection limit, good repeatability, and good excellent selectivity for common interfering substances.

2. Materials and Methods

2.1. Preparation of Co$_3$O$_4$ NNs/NF. Pretreatment of Ni Foam: firstly, an area of $2 \times 4$ cm$^2$ Ni foam was sonicated in the HCl solution (2 M), anhydrous ethanol, deionized water for 15 min, respectively, and then, the cleaned Ni foam was dried at 60°C.

Preparation of Co$_3$O$_4$ NNs/NF: 5 mmol of Co(N-O$_2$)$_3$·6H$_2$O and 4.5 mmol of urea were solved into 30 mL of deionized water. After stirring, 2 mmol of cetyltrimethyl ammonium bromide (CTAB) was added into the above solution and stirred at 45°C for 30 min. Subsequently, the uniform solution was transferred into the Teflon-sealed autoclave, and the cleaned Ni foam was inserted into the inner container by tweezers, and the Ni foam was completely immersed in the solution. Then the autoclave was sealed and placed in the electric hot air drying oven, and then heated continuously for 6 h at 120°C. When the autoclave naturally cooled to room temperature, the autoclave was opened, and the Ni foam with precursor was collected by tweezers and washed repeatedly with ethanol and distilled water. Then, the Ni foam was put it into a drying oven with a temperature set at 60°C for 8 h. Finally, the Ni foam with precursor was placed in a clean crucible and then baked in a muffle furnace. The heating rate was set at 1°C/min, heated to 350°C, and continuously calcined 2 h.

2.2. Electrochemical Performance Test. In current work, we prepared the sensing material on the surface of Ni foam. The thickness of sensing film is about 0.1 mm. During the electrochemical test, the RST-5000F electrochemical workstation was used for electrochemical test. The freshly prepared NaOH (0.1 M) solution was served as the electrolyte. Cyclic voltammetry and chronoamperometry were performed at room temperature. Co$_3$O$_4$ NNs/NF (1 × 2 cm$^2$), Ag/AgCl electrode, and Pt sheet electrode were used as working electrode, reference electrode, and counter electrode, respectively. The humidity in current work is 30 RH%.

3. Results and Discussion

The prepared sample was obtained from the Ni foam by ultrasonic wave, and the composition of the sample was studied by XRD. The XRD pattern of Co$_3$O$_4$ arrays on Ni foam is shown in Figure 1. The obvious diffraction peaks at 19.0°, 31.2°, 36.8°, 38.5°, 44.8°, 55.6°, 59.3°, and 65.2° are corresponding to (111), (220), (311), (222), (400), (422), (511), and (440) planes of cubic phase Co$_3$O$_4$ (JCPDS No. 42-1467). Moreover, no other impurity peaks are found in the pattern, which indicates that the as-prepared Co$_3$O$_4$ sample has good crystallinity and high purity.

Figure 2(a) displays the SEM image of Co$_3$O$_4$ NNs/NF electrode at low magnification. It can be seen that Co$_3$O$_4$ nanoneedles are evenly covered on the conductive substrate, and there is a gap between the nanoneedles, which is conducive to the diffusion of electrolyte and the escape of bubbles on the electrode surface, so as to improve the catalytic activity. From the high magnified SEM image in Figure 2(b), it can be found that the diameter of Co$_3$O$_4$ nanoneedles is about 80-100 nm, and its surface is rough and uneven, which may be porous structure. Subsequently, Co$_3$O$_4$ nanoneedles were dispersed in ethanol by ultrasonic method and characterized by TEM technique. Figure 2(c) shows that the nanoneedles with a diameter of about 100 nm are actually composed of interconnected single nanoparticles, which is consistent with the SEM observation. Such highly porous nanoneedle structure is helpful for the rapid diffusion of electrolyte ions in the electrode and accelerates electron transfer, so that the as-prepared Co$_3$O$_4$ electrode may have good electrochemical performance. Additionally, the HR-TEM image of Co$_3$O$_4$ nanoneedles (Figure 2(d)) shows that there are two groups of clear lattice fringes. It is found that their fringe spacing is 0.242 nm and 0.465 nm, respectively, which exactly corresponds to the (311) and (111) crystal planes of Co$_3$O$_4$ standard diffraction spectrum (JCPDS 42-1467). These results further confirm the successful synthesis of porous Co$_3$O$_4$ nanoneedles on Ni foam.

Using a typical three electrode system, the electrocatalytic activity of Co$_3$O$_4$ NNs/NF for glucose oxidation was investigated by cyclic voltammetry. Figure 3(a) shows the CV curve of Co$_3$O$_4$ NNs/NF in the absence and presence of 0.6 mM glucose at a scanning speed of 10 mV s$^{-1}$. Obviously, the oxidation peak current of Co$_3$O$_4$ NNs/NF at 0.55 V increases significantly after the addition of 0.6 mM glucose. In addition, Figure 3(b) shows the CV curve of Co$_3$O$_4$ NNs/NF when the glucose concentration in 0.1 M, the NaOH solution is 0 mM, 0.2 mM, 0.4 mM, and 0.6 mM, respectively (the scanning speed is set to 10 mV s$^{-1}$). With the increase of glucose concentration, the peak current also increases. The above results show that the prepared Co$_3$O$_4$ NNs/NF has good electrocatalytic activity for glucose oxidation, and the specific process can be described as [15, 16]

\[
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \rightarrow 3\text{CoOOH} + e^- ,
\]

\[
\text{CoOOH} + \text{OH}^- \rightarrow \text{Co}_2\text{O}_3 + \text{H}_2\text{O} + e^- ,
\]

\[
2\text{Co}_2\text{O}_3 + \text{glucose} \rightarrow 2\text{CoOOH} + \text{gluconolactone} .
\]
Figure 1: XRD pattern of Co$_3$O$_4$ NNs.

Figure 2: SEM images of Co$_3$O$_4$ NNs/NF at (a) low magnification and (b) high magnification. (c) TEM and (d) HR-TEM images of Co$_3$O$_4$ NNs.
oxidation process of glucose on Co$_3$O$_4$ NNs/NF is a diffusion controlled process [17].

Chronoamperometry technology was carried out to evaluate the sensitivity, detection limit, and selectivity of the electrode to glucose. Under the condition of working voltage of 0.55 V, Co$_3$O$_4$ NNs/NF electrode was tested, and glucose solutions with different concentrations were gradually added to 0.1 M NaOH solution. As shown in Figure 4(a), when glucose of different concentrations is added to the alkaline solution in the state of uniform stirring at an interval of 50 s, it can be seen that the current response is relatively rapid and the curve is similar to a ladder. In addition, Figure 4(b) shows the corresponding relationship between glucose concentration and current in this process. In the range of 1 μM-0.338 mM, the concentration and current have good linear correlation. Its linear regression equation can be expressed as $I (\text{mA}) = 9.14C (\text{mM}) + 0.097$ ($R^2 = 0.99017$), and the sensitivity is 4570 μA mM$^{-1}$ cm$^{-2}$. The detection limit (LOD) for glucose is about 0.91 μM ($S/N = 3$), and its response time is about 8 s (Figure 4(c)).

Since there are other interfering substances in real human serum, which may also be oxidized, it is necessary to test the anti-interference ability of Co$_3$O$_4$ NNs/NF electrode. Here, the typical disruptors were selected, such as uric acid (UA), ascorbic acid (AA), fructose, and sucrose for electrochemical detection by chronoamperometry. Because the concentration of blood glucose in normal human serum is 30-50 times that of these interfering substances [18], 1.0 mM glucose and 0.1 mM interfering substances were added for testing. It can be seen from Figure 4(d) that the current density increases significantly after adding 1.0 mM glucose, but there is no significant change in current density after adding other interferents. Therefore, Co$_3$O$_4$ NNs/NF has good selectivity for glucose detection.

Repeatability and stability are also important indicators to evaluate the operability and durability of the prepared nonenzymatic glucose sensor electrode. Five Co$_3$O$_4$ NNs/NF electrodes were prepared by the same method, and the prepared electrodes were tested by cyclic voltammetry under the same conditions. Their respective peak oxidation...
Figure 4: (a) The amperometric response of Co$_3$O$_4$ NNS/NF when glucose was continuously injected into 0.1 M NaOH solution at 0.55 V; the inset showed the enlarged response curve from the black rectangle. (b) Calibration curve between current response and glucose concentration. (c) The response time of Co$_3$O$_4$ NNS/NF. (d) The amperometric response of Co$_3$O$_4$ NNS/NF to the sequential addition of 1 mM glucose and 0.1 mM different interferents (UA, AA, fructose, and sucrose); Potential: 0.55 V. (e) The peak oxidation currents of Co$_3$O$_4$ NNS/NF fabricated in five batches via the same method. (f) Storage stability of Co$_3$O$_4$ NNS/NF tested by CV.
4. Conclusions
In this work, a simple one-step hydrothermal synthesis method of Co$_3$O$_4$ NNs/NF is proposed for the detection of nonenzymatic glucose. The sensor based on Co$_3$O$_4$ NNs/NF has good sensitivity to glucose (4570 $\mu$A mM$^{-1}$ cm$^{-2}$) and low detection limit (0.91 $\mu$M). The linear detection range is 1 $\mu$M-0.337 mM. Moreover, it has good selectivity and stability for glucose. At the 28th day, its oxidation response current still maintains 87.1% of its initial value. The good electrochemical sensing performance of Co$_3$O$_4$ NNs/NF based sensor for glucose can be attributed to the following factors: on the one hand, the firm and evenly arranged Co$_3$O$_4$ nanoneedles grown directly on the conductive substrate can prevent the blockage of active sites caused by additional adhesives, so as to ensure efficient electron transfer. On the other hand, the ordered and interconnected porous structure and large specific surface area can not only provide more active sites for electrochemical reactions but also enhance the contact between active substances.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

Acknowledgments
This work was supported by the Natural Science Foundation of Chongqing (Grant No. 2022NSCQ-MSX4128).

References
[1] R. Wilson and A. P. F. Turner, "Glucose oxidase: an ideal enzyme," Biosensors and Bioelectronics, vol. 7, no. 3, pp. 165–185, 1992.
[2] A. Meng, X. Yuan, Z. Li, K. Zhao, L. Sheng, and Q. Li, "Direct growth of 3D porous (Ni- Co)$_3$S$_2$ nanosheets arrays on rGO-PEDOT hybrid film for high performance non-enzymatic glucose sensing," Sensors and Actuators B: Chemical, vol. 291, no. 15, pp. 9–16, 2019.
[3] Q. Dong, H. Ryu, and Y. Lei, "Metal oxide based non-enzymatic electrochemical sensors for glucose detection," Electrochimica Acta, vol. 370, no. 20, article 137744, 2021.
[4] W. B. Kim, S. H. Lee, M. Cho, and Y. Lee, "Facile and cost-effective CuS dendrite electrode for non-enzymatic glucose sensor," Sensors and Actuators B: Chemical, vol. 249, pp. 161–167, 2017.
[5] R. Wang, X. Liu, Y. Zhao et al., "Novel electrochemical non-enzymatic glucose sensor based on 3D Au@Pt core-shell nanoparticles decorated graphene oxide/multi-walled carbon nanotubes composite," Microchemical Journal, vol. 174, article 107061, 2022.
[6] Y. Fan, X. Tan, X. Ou, S. Chen, and S. Wei, "An ultrasensitive electrochemiluminescence biosensor for the detection of concanavalin A based on Au nanoparticles-thiosemicarbazide functionalyzed PtNi nanocubes as signal enhancer," Biosensors and Bioelectronics, vol. 87, no. 15, pp. 802–806, 2017.
[7] M. Usman, L. Pan, A. Farid et al., "Ultra-fast and highly sensitive enzyme-free glucose sensor based on 3D vertically aligned silver nanoplates on nickel foam-graphene substrate," Journal of Electroanalytical Chemistry, vol. 848, no. 1, article 113342, 2019.
[8] M. Chen, W. Li, L. Chen, S. Ren, and D. Han, "NiCo-LDH nanoflake arrays-supported nanoparticles on copper foam as a highly sensitive electrochemical non-enzymatic glucose sensor," Analytica Chimica Acta, vol. 1177, no. 8, article 338787, 2021.
[9] D. W. Hwang, S. Lee, M. Seo, and T. D. Chung, "Recent advances in electrochemical non-enzymatic glucose sensors - a review," Analytica Chimica Acta, vol. 1033, no. 29, pp. 1–34, 2018.
[10] D. Ge, Y. Yang, X. Ni et al., "Self-template formation of porous Co3O4hollow nanoprisms for non-enzymatic glucose sensing in human serum," RSC Advances, vol. 10, no. 63, pp. 38369–38377, 2020.
[11] X. Niu, Y. Li, J. Tang, Y. Hu, H. Zhao, and M. Lan, "Electrochemical sensing interfaces with tunable porosity for nonenzymatic glucose detection: A Cu foam case," Biosensors and Bioelectronics, vol. 51, no. 15, pp. 22–28, 2014.
[12] L. Jiang, S. Gu, Y. Ding, F. Jiang, and Z. Zhang, "Facile and novel electrochemical preparation of a graphene-transition metal oxide nanocomposite for ultrasensitive electrochemical sensing of acetaminophen and phenacetin," Nanoscale, vol. 6, no. 1, pp. 207–214, 2014.
[13] M. Yang, J. M. Jeong, K. G. Lee, D. H. Kim, S. J. Lee, and B. G. Choi, "Hierarchical porous microspheres of the Co$_3$O$_4$@graphene with enhanced electrocatalytic performance for electrochemical biosensors," Biosensors and Bioelectronics, vol. 89, Part 1, pp. 612–619, 2017.
[14] W. Li, D. Liu, X. Feng, Z. Zhang, X. Jin, and Y. Zhang, "High-performance ultrathin Co3O4 nanosheet supported PdO/Co3O4 catalysts for methane combustion," Advanced Energy Materials, vol. 9, no. 18, article 1803583, 2019.
[15] A. T. E. Villan, B. Dinesh, M. Rethinasabapathy et al., "Hexagonal Co3O4anchored reduced graphene oxide sheets for high-performance supercapacitors and non-enzymatic glucose sensing," Journal of Materials Chemistry A, vol. 6, no. 29, pp. 14367–14379, 2018.
[16] M. Zheng, L. Li, P. Gu, Z. Lin, H. Xue, and H. Pang, "A glassy carbon electrode modified with ordered nanoporous Co$_3$O$_4$ for non-enzymatic sensing of glucose," Microchimica Acta, vol. 184, no. 3, pp. 943–949, 2017.
[17] D. Yin, X. Bo, J. Liu, and L. Guo, “A novel enzyme-free glucose and H₂O₂ sensor based on 3D graphene aerogels decorated with Ni₃N nanoparticles,” *Analytica Chimica Acta*, vol. 1038, pp. 11–20, 2018.

[18] I. U. Hassan, H. Salim, G. A. Naikoo et al., “A review on recent advances in hierarchically porous metal and metal oxide nanostructures as electrode materials for supercapacitors and non-enzymatic glucose sensors,” *Journal of Saudi Chemical Society*, vol. 25, no. 5, article 101228, 2021.