Supporting Information

A disposable and sensitive non-enzymatic glucose sensor based on 3D-Mn doped NiO nano-flower modified flexible electrode

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Experimental section

Materials

Carbon cloth (CFC) was obtained from TORAY Japan. Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) was purchased from the Kelon Chemical Reagent Factory (Chengdu, China). Manganese chloride tetrah ($MnCl_2 \cdot 4H_2O$) and hexamethylene tetramine ($C_6H_{12}N_4$) were bought from the Cologne Chemicals Co. Ltd (Chengdu, China). Absolute ethanol (C_2H_5OH), acetone (CH_3COCH_3) and urea were purchased from the Chuandong Chemical Industry Group (Chongqing, China). Sodium hydroxide (NaOH) was bought from the Sinopharm Chemical Reagent Co. Ltd. Glucose (Glu) was purchased from ACROS. Ascorbic acid (AA), acetylsalicylic acid (ASA), acetaminophen (AMP), NaCl and glycine (Gly) were obtained from Sigma-Aldrich (St. Louis, USA). Dopamine hydrochloride (DA) was purchased from the Yuancheng Chemical Co. Ltd (Wuhan, China). Ultrapure water was produced from a Milli-Q system (18.25 MΩ cm^{-1}).

Characterization

The structure of the as-prepared Bare CFC, NiO/CFC and Mn-NiO/CFC was characterized by a Nova 400 scanning electron microscope (SEM). The element content and composition of the electrode materials were analyzed quantitatively and qualitatively by EDS. The x-ray diffraction (XRD) analysis was performed using Bruker AXS D5005 to obtain the crystal structure and phrase information of the samples. The chemical composition and electronic structure of samples were conducted on an ESCALAB250Xi X-ray photoelectron spectroscopy (XPS).

Electrochemical measurements

A CHI 760E (Shanghai, CH Instruments, Inc.) electrochemical workstation was used to conduct all electrochemical measurements. A conventional three-electrode system was employed for the experiments, with the as-prepared Mn-NiO/CFC as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (3 M KCl) as the reference electrode. The techniques of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Amperometric i-t curves were applied to investigate the electrochemical performance of the prepared Mn-NiO/CFC electrode in 100 mM NaOH

solution or 10 mL 5 mM·L^{-1} $[Fe(CN)_6]^{3-/4-}$ solution (including 0.1 M KCl). In addition, all tests were performed at room temperature.

Electrochemical characterization

The conductivity of the bare CFC, NiO/CFC and Mn-NiO/CFC electrodes was tested by CV and EIS in 10 mL 5 mM·$L^{-1}$$[Fe(CN)_6]^{3-/4-}$ solution (including 0.1 M KCl). The CVs were carried out at a scan rate 50 mV/s from -0.2 V to 0.6 V. The frequency range investigated by EIS was 10^{-1} to 10^5 Hz. The glucose catalytic performance of the three electrodes was tested by amperometry in 10 mL NaOH with adding 150 μM glucose every 50 s for seven times. The CVs of Mn-NiO/CFC at different scan rate (25-500 mV/s) were recorded to investigate the reaction kinetics. Furthermore, the scanning potential of CVs varied from 0 to 0.8V, and the scan rate was 50 mV/s.

Optimization

CVs were conducted by dropping 1 mM glucose into different concentrations of NaOH solutions (25, 50, 75, 100, 125, 150 mM) to obtain the optimal concentration of NaOH. The electrocatalytic performance of Mn-NiO/CFC to different concentrations of glucose (0, 1, 2, 4, 6 mM) was tested with CV at optimal concentrations, with a scan rate 50 mV/s from 0.2 V to 1.0 V. The optimal working potential and preparation calcination time of the electrode materials were obtained through comparing a series of potentials by adding 150 μM glucose continuously for seven times.

Linear detection research

At the optimal working potential of 0.6 V, the linear study of the electrode was carried out by amperometry in 10 mL 100 mM NaOH solution system with continuously adding different concentrations of glucose every 50 s, three times for each concentration.

Selectivity and reproducibility study of the Mn-NiO/CFC

Under the optimal experimental conditions, selectivity of the Mn-NiO/CFC was evaluated with continuously adding 500 μM glucose and 50 μM biological interfering species such as AA, UA, Fru, Suc, urea and DA by using amperometic method. The reproducibility of this sensor was confirmed at 0.6 V via assessing the current response of 150 μM glucose at five Mn-NiO/CFC electrodes prepared by the same way. Each electrode was repeated three times.

Figure S1:

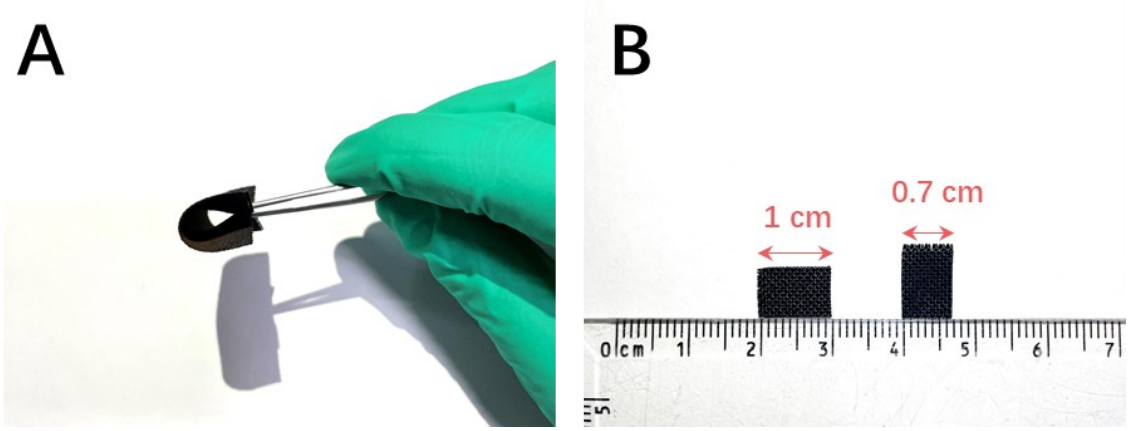

Figure S1 (A) Images of the prepared flexible CFC (5×5 cm^2); the CFCs with a size of 1×0.7 cm^2

Figure S2:

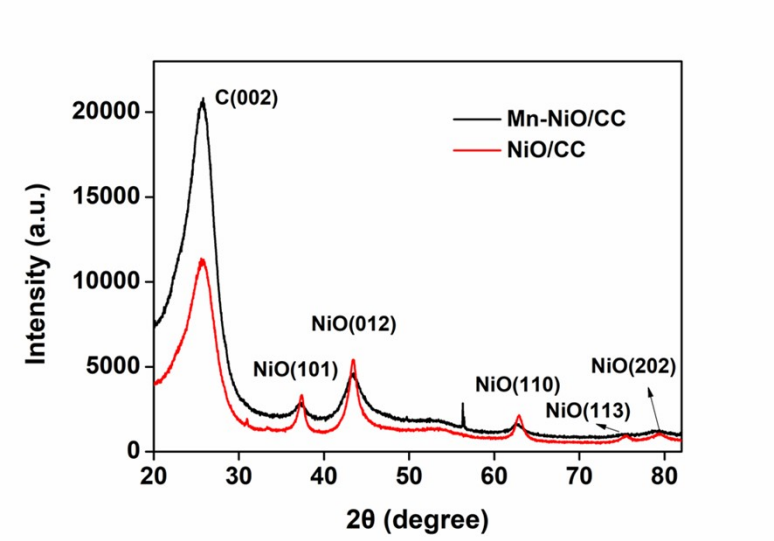

Figure S2 XRD patterns for the Mn-NiO/CFC and NiO/CFC

Figure S3:

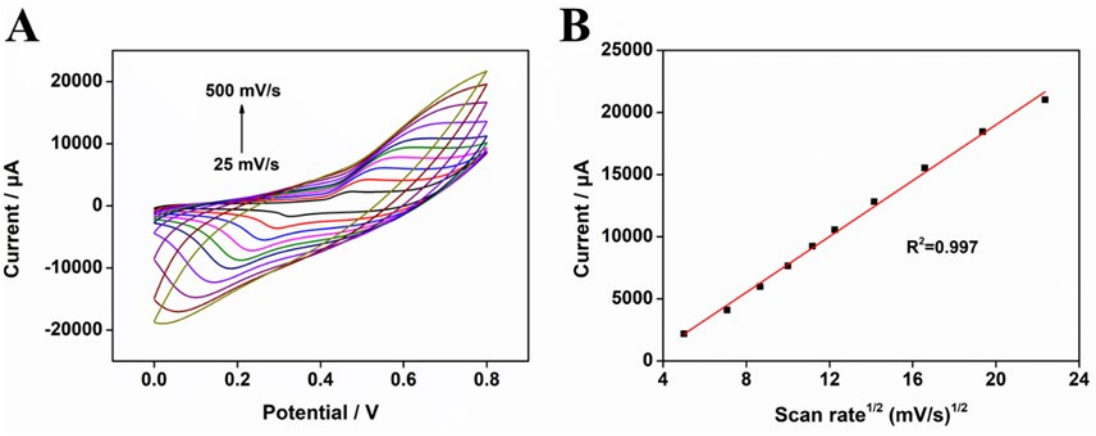

Figure S3 (A) CVs of the Mn-NiO/CFC at different scan rates (solution: 100 mM NaOH containing 1 mM glucose); (B) The linear fitting diagram of its oxidation peak current and the square root of the sweep speed.

Table S1 Comparison of the performance of Mn-NiO /CFC sensor electrode and other sensors of the similar type for glucose detection.

Electrode materials	Linear range（μM）	LOD（μM）	Documents
Ni_7S_6/NiO	90-3120	0.3	[1]
Ni/$Cu(OH)_2$ NS	10-1490	1.27	[2]
Ni/Co-TCPP MOFs	1-3800	0.3	[3]
Ni/PANI coaxial nanowires	0-7000	10	[4]
CuO polyhedrons/CFC	0.5-800	0.46	[5]
Co_3O_4/CuO NRA/CFC	1-500	0.38	[6]
MOF-74(Cu) NS-CFC	1-1000	0.41	[7]
CuO/$Ni(OH)_2$/CFC	50-8500	0.31	[8]
$CuCo_2O_4$@$NiCo_2O_4$/CFC	1-1158	0.35	[9]
GCE/WMCNT/ZnO NPs	100~10000	0.82	[10]
GCE/CuO NWs-MoS_2/Au NPs	0.5~5670	0.5	[11]
GCE/Hollow cage-like NiO	0.1~5000	0.1	[12]
Cu_3Se_2 film	2.8~1500	2.8	[13]
GCE/Cu/ZnO NC	10~7000	57	[14]
GCE/MXene-Cu_2O	10~30000	2.83	[15]
Mn-NiO/CFC	3-5166	0.28	This work

Figure S4:

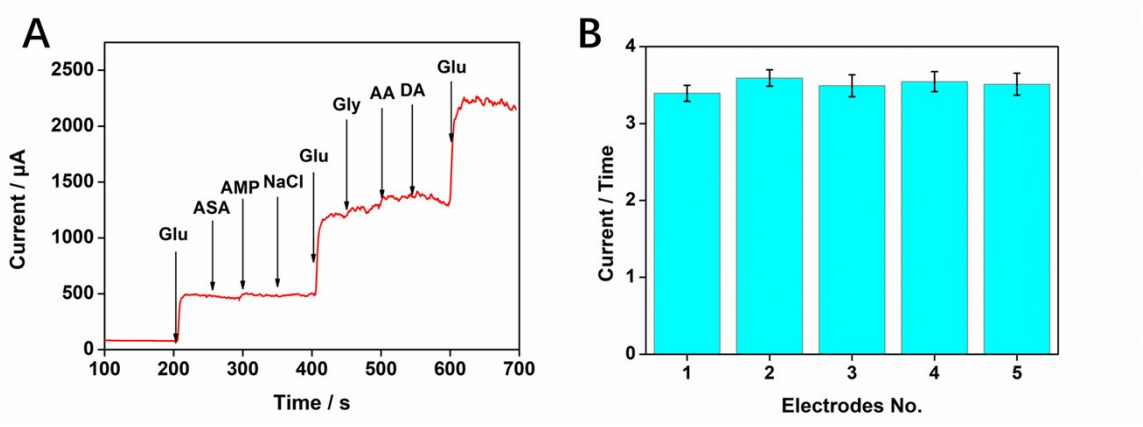

Figure S4 (A) Amperometric response of the the Mn-NiO/CFC to the selectivity of glucose; **(B)** Reproducibility of five Mn-NiO/CFC electrodes. (The error bar was calculated based on the standard deviation of 3 measurements, n=3)

Figure S5:

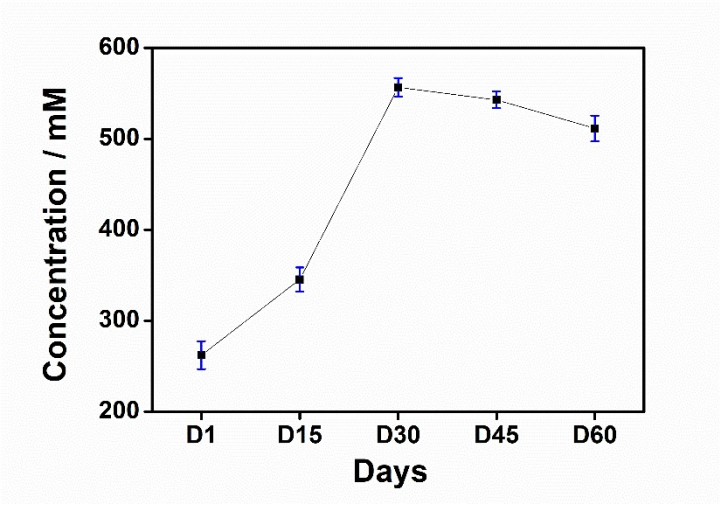

Figure S5 Determination of glucose in sorghum fermentation broth of different cycle by Mn-NiO/CFC sensors. (The error bar was calculated based on the standard deviation of 3 measurements, n=3)

REFERENCES

1. Z. Tan, Y. Huang, S. Wang, C. Feng, Z. Sun, H. Wu and Y. Zhang, *Ionics*, 2019, **25**, 3961-3969.
2. T. Zhe, X. Sun, Y. Liu, Q. Wang, F. Li, T. Bu, P. Jia, Q. Lu, J. Wang and L. Wang, *Microchemical Journal*, 2019, **151**.
3. S. Li, X. Zhan, W. Bai and J. Zheng, *Journal of The Electrochemical Society*, 2020, **167**.
4. H. Wang, J. Qiu, S. Sun, W. Zhang and S. Yao, *Journal of Materials Science: Materials in Electronics*, 2021, **32**, 7751-7764.
5. S. Cheng, X. Gao, S. DelaCruz, C. Chen, Z. Tang, T. Shi, C. Carraro and R. Maboudian, *J Mater Chem B*, 2019, **7**, 4990-4996.
6. S. Cheng, S. DelaCruz, C. Chen, Z. Tang, T. Shi, C. Carraro and R. Maboudian, *Sensors and Actuators B: Chemical*, 2019, **298**.
7. S. Hu, Y. Lin, J. Teng, W. L. Wong and B. Qiu, *Mikrochim Acta*, 2020, **187**, 670.
8. S. Sun, N. Shi, X. Liao, B. Zhang, G. Yin, Z. Huang, X. Chen and X. Pu, *Applied Surface Science*, 2020, **529**.
9. S. Liu, W. Zeng, Q. Guo and Y. Li, *Nanotechnology*, 2020, **31**, 495708.
10. A. Tarlani, M. Fallah, B. Lotfi, A. Khazraei, S. Golsanamlou, J. Muzart and M. Mirza-Aghayan, *Biosens Bioelectron*, 2015, **67**, 601-607.
11. J. Bao, Y. L. Qi, D. Q. Huo, J. Z. Hou, X. T. Geng, M. Samalo, Z. S. Liu, H. B. Luo, M. Yang and C. J. Hou, *J Electrochem Soc*, 2019, **166**, B1179-B1185.
12. Z. H. Ibupoto, A. Nafady, R. A. Soomro, Sirajuddin, S. T. H. Sherazi, M. I. Abro and M. Willander, *Rsc Adv*, 2015, **5**, 18773-18781.
13. D. B. Malavekar, S. B. Jadhav, S. B. Kale, U. M. Patil and C. D. Lokhande, *Mater Today Sustain*, 2022, **20**.
14. A. El Golli, M. Echabaane and C. Dridi, *Mater Chem Phys*, 2022, **280**.
15. T. S. Gopal, S. K. Jeong, T. A. Alrebdi, S. Pandiaraj, A. Alodhayb, M. Muthuramamoorthy and A. N. Grace, *Mater Today Chem*, 2022, **24**.