

Electronic Supplementary Information

High-performance non-enzymatic glucose detection: using conductive Ni-MOF as an electrocatalyst

Yanxia Qiao,^a Qian Liu,^b Siyu Lu,^c Guang Chen,^d Shuyan Gao,^e Wenbo Lu^{a*} and
Xuping Sun^{b*}

^a Key Laboratory of Magnetic Molecules and Magnetic Information Materials (Ministry of Education), School of Chemistry and Material Science, Shanxi Normal University, Linfen 041004, China. E-mail: luwb@sxnu.edu.cn

^b Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, Sichuan, China. E-mail: xpsun@uestc.edu.cn

^c Green Catalysis Center and College of Chemistry, Zhengzhou University, Zhengzhou 450001, Henan, China

^d The Key Laboratory of Life-Organic Analysis and Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, China

^e School of Materials Science and Engineering, Henan Normal University, Xinxiang 453007, Henan, China

Experimental section

Materials

Fructose (Fru) and glucose (Glu) were purchased from Beijing Chemical Works. 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), N,N-Dimethylformamide (DMF), Nickel acetate tetrahydrate ($\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$), ascorbic acid (AA), Urea, NaCl, L-cysteine (L-Cys), lactose (Lac), uric acid (UA) and dopamine (DA) were purchased from Aladdin Ltd. (Shanghai, China). All reagents were used as received without further purification. The water use throughout all experiments was purified through a Millipore system.

Preparation of conductive Ni-MOF

In a typical procedure, HHTP (0.02 mmol) and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.04 mmol) were added were added in 1 mL solvent mixture of water/DMF (v: v = 1:1) under sonication for 20 min in a 20 mL glass vial. The reaction mixture was then heated in an oven at 85 °C for 15 h. After cooling down to room temperature, the reaction product was centrifuged and the solid precipitate was washed with ultrapure water and alcohol. The resulting black powder was transferred into a glass vial and dried overnight under vacuum at 75 °C

Preparation of human blood serum

The human blood was put into 45 °C water bath for 10 minutes and then centrifuged at 4000 r/min for 5 minutes. Human blood serum was obtained by collected the supernate. The disposed serum is kept in −5 °C to −20 °C.

Characterizations

Powder X-ray diffraction (XRD) data were acquired on a RigakuD/MAX 2550 diffractometer with Cu K α radiation ($\lambda=1.5418 \text{ \AA}$). Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an

ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements

Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a conventional three electrode system, using the conductive Ni-MOF as working electrode, the platinum wire as counter electrode and Ag/AgCl as reference electrode. All tests were carried out at room temperature.

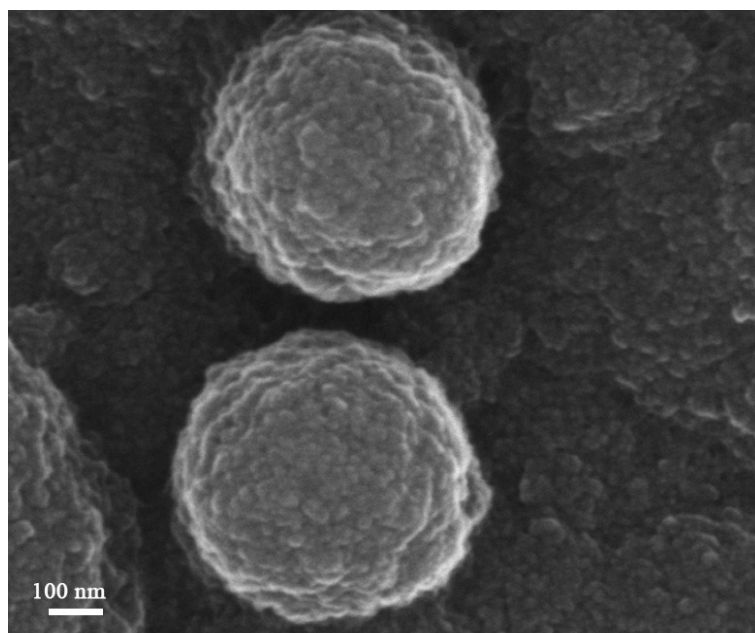


Fig. S1. SEM image for the conductive Ni-MOF.

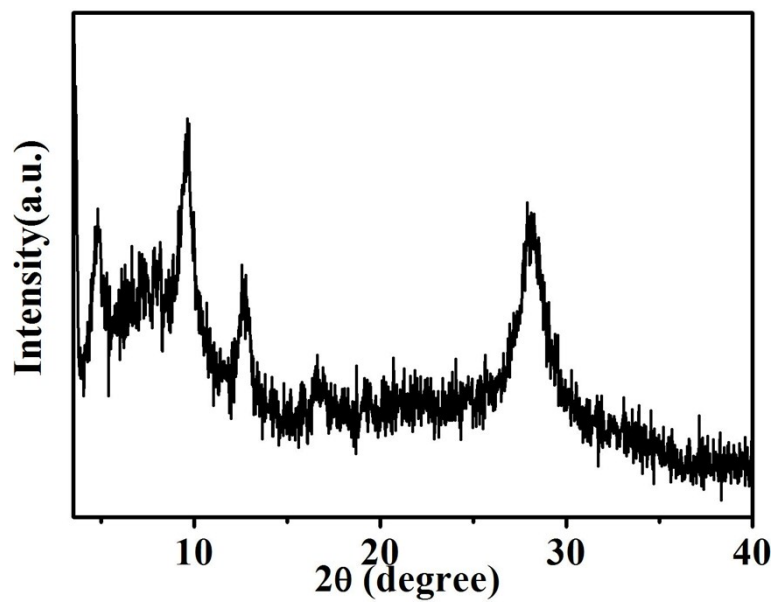


Fig. S2. XRD pattern for the conductive Ni-MOF after long term stability tests.

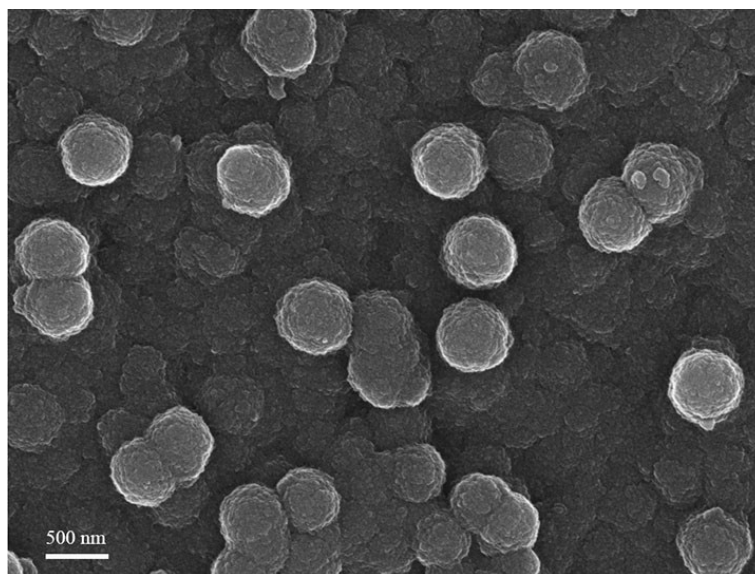


Fig. S3. SEM image for the conductive Ni-MOF after long-term stability tests.

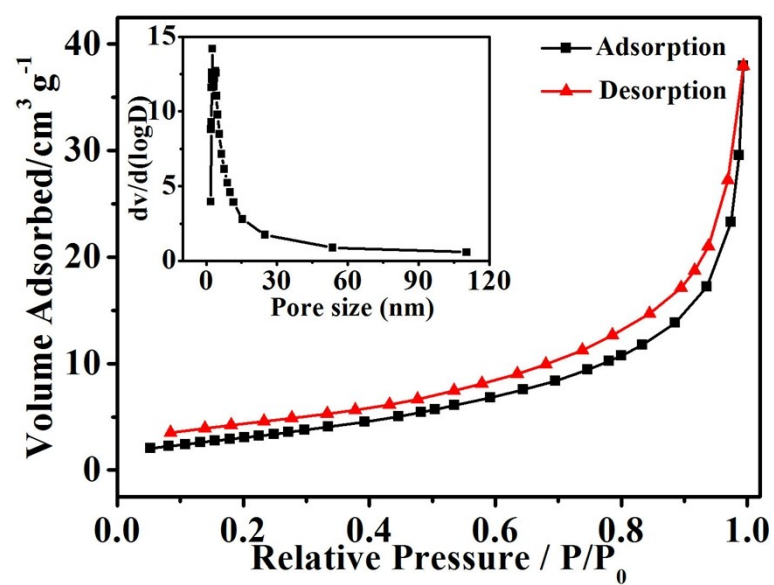


Fig. S4. Nitrogen adsorption/desorption isotherms and pore size distribution (inset) of the conductive Ni-MOF.

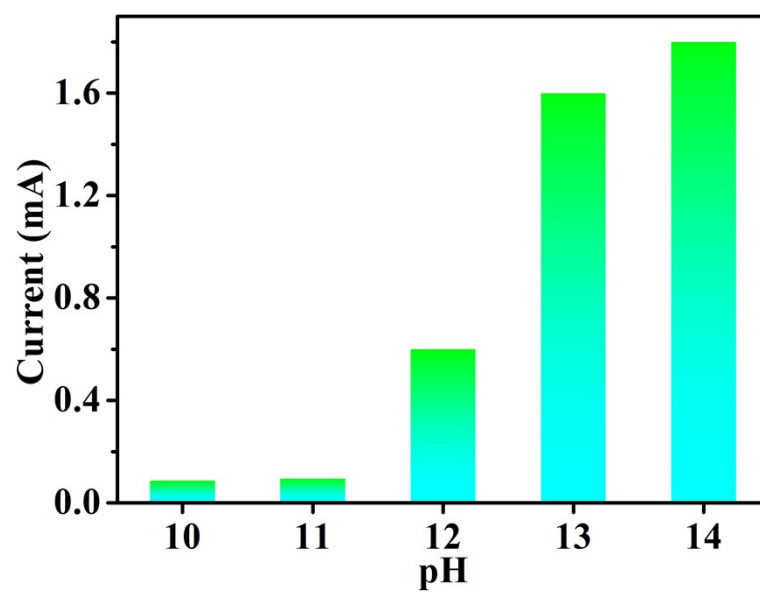


Fig. S5. Influence of pH on the current response of the conductive Ni-MOF with 1 mM glucose (scan rate: 20 mV/s).

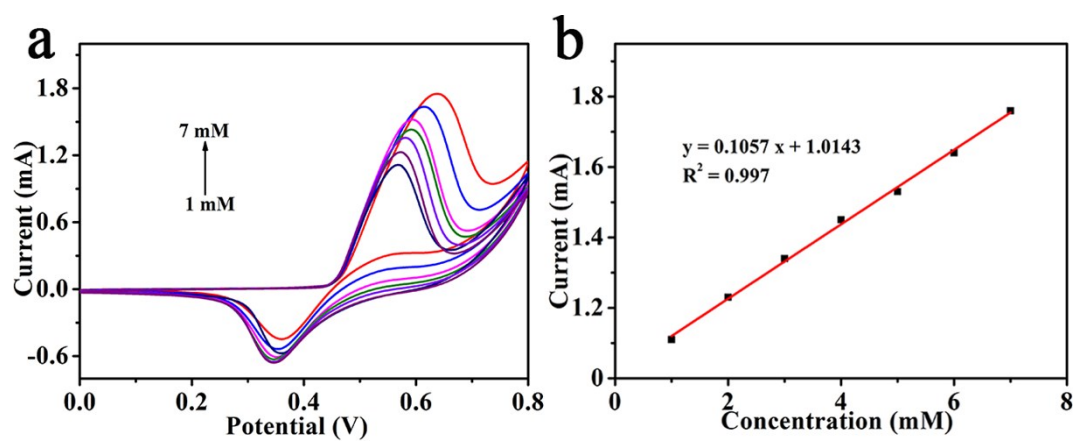


Fig. S6. (a) CV curves of samples where different glucose concentrations from 1 to 7 mM added into NaOH solution containing 20% of peach juice (scan rate: 20 mV/s). (b) Calibration curve of oxidation peak current response to the concentration of glucose.

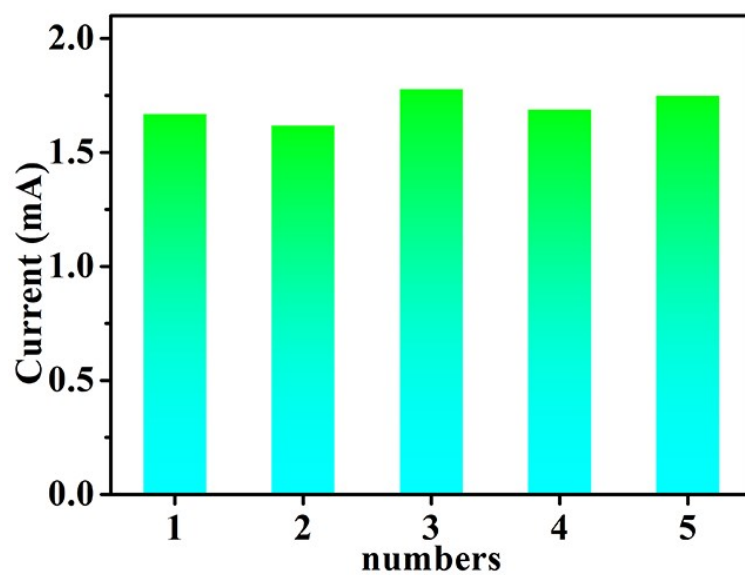


Fig. S7. Reproducibility of 5 sensors towards 1 mM glucose in 0.1 M NaOH.

Table S1. Performance comparison of non-enzymatic glucose electrochemical sensors using different catalyst materials.

Catalysts	Sensitivity($\mu\text{A mM}^{-1} \text{ cm}^{-2}$)	Linear range (mM)	Detection limit	Ref.
Conductive Ni-MOF	21744	0.001-8	0.66	This work
Ni(OH) _x /CC	19420 \pm 70	0.004-0.6	0.47	1
Ni/Cu(OH) ₂	8722	0.01-1.490	1.27	2
Ni ₃ (PO ₄) ₂ @ZIF-67	2783	0.001-4.0	0.7	3
Ni ₂ P NA/CC	7792	0.001-3.0	0.18	4
Ni-B/NF	8250	0.005-2.66	5	5
CPO-27-Ni ^{II}	40.95	0.04-6	1.46	6
Ni-MIL-77 NBs	1.542	0.001-0.5	0.25	7
Ni(OH) ₂ @PEDOT-rGO	346	0.002-7.1	0.6	8
NiCoP	14586	-	0.13	9
Ni-MOF/MWCNT	685	0.01-1.12	0.003	10
Ni(TPA)-SWCNT-CS	-	0.02-4.4	4.6	11
rGO/Ni(OH) ₂	11400	0.015-30	15	12
Ni-Co-S/TM	3291.5	0.001-3	0.12	13

Table S2. Blood glucose levels of human serum samples offered by hospital and those determined by conductive Ni-MOF electrode.

Sample	Measured by medical equipment (mM)	Measured by conductive Ni-MOF (mM)	RSD(%)	Bias(mM)
1	3.10	3.25	3.34	0.15
2	4.90	4.86	1.83	-0.04
3	6.60	6.69	0.96	0.09

The medical equipment is the blood glucose meter (Yuwell, model: 580, Yuwell-Jiangsu Yuyue medical equipment & supply Co., Ltd.).

Reference

- 1 Q. Wa, W. Xiong, R. Zhao, Z. He, Y. Chen and X. Wang, *ACS Appl. Nano Mater.*, 2019, **2**, 4427–4434.
- 2 T. Zhe, X. Sun, Y. Liu, Q. Wang, F. Li., T. Bu, P. Jia, Q. Lu, J. Wang and L. Wang, *Microchem. J.*, 2019, **151**, 104197.
- 3 L. Xiao, Q. Zhao, L. Jia, Q. Chen, J. Jiang and Q. Yu. *Electrochim. Acta*, 2019, **304**, 456–464.
- 4 T. Chen, D. Liu, W. Lu, K. Wang, G. Du, A. M. Asiri and X. Sun, *Anal. Chem.*, 2016, **88**, 7885–7889.
- 5 M. Wang, D. He, M. Huang, X. Wang and P. Jiang, *J. Alloys Compd.*, 2019, **786**, 530–536.
- 6 N. S. Lopa, M. M. Rahman, F. Ahmed, S. C. Sutradhar, T. Ryu and W. Kim, *J. Electroanal Chem.*, 2018, **822**, 43–49.
- 7 X. Xiao, S. Zheng, X. Li, G. Zhang, X. Guo, H. Xue and H. Pang, *J. Mater. Chem. B.*, 2017, **5**, 5234–5239.
- 8 L. Shenga, Z. Li, A. Meng and Q. Xu, *Sens. Actuators B: Chem.*, 2018, **254**, 1206–1215.
- 9 Z. Wang, X. Cao, D. Liu, S. Hao, G. Du, A. M. Asiri and X. Sun, *Chem. Commun.*, 2016, **52**, 14438–14441.
- 10 T. Q. N. Tran, G. Das and H. H. Yoon, *Sens. Actuators B: Chem.*, 2017, **243**, 78–83.
- 11 F. Wang, X. Chen, L. Chen, J. Yang and Q. Wang, *Mater. Sci. Eng. C*, 2019, **96**, 41–50.
- 12 P. Subramanian, J. Niedziółka-Jönsson, A. Lesniewski, Q. Wang, M. Li, R. Boukherroub and S. Szunerits, *J. Mater. Chem. A*, 2014, **2**, 5525–5533.
- 13 X. Cao, K. Wang, G. Du, A. M. Asiri, Y. Ma, Q. Lu and X. Sun, *J. Mater. Chem. B*, 2016, **4**, 7540–7544.