Electronic Supplementary Material (ESI) for Analytical Methods.

A Sensitive Enzyme-Free Electrochemical Sensor Based on Rod-Shaped Bimetallic MOF Anchored on Graphene Oxide Nanosheets for Determination of Glucose in *Huangshui*

Yi Ma[a,1,*] , Yinjiang Leng[a,1], Danqun Huo [b], Dong Zhao [c] , Jia Zheng [c], Huisi Yang[b], Peng Zhao[b] , Feifeng Li[a] , Changjun Hou [a,b,*]

[a] College of Biological Engineering, Sichuan University of Science and Engineering, 188 University Town, Yibin, China

[b] Chongqing Univ, Bioengn Coll, State & Local Joint Engn Lab Vasc Implants, Minist Educ,Key Lab Biorheol Sci & Technol, Chongqing , China

[c] Wuliangye Yibin Co., Ltd, Yibin, Sichuan,China

[1] These authors contributed equally to this work.

Corresponding authors: zhangyer2008@suse.edu.cn; houcj@cqu.edu.cn

S1. Materials and Instruments

Graphite powder were purchased from Sigma-Aldrich (St. Louis, USA). $NiCl_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, p-phthalic acid(PTA), N, N-dimethylformamide(DMF), were purchased from Adamas Reagent Co.Ltd. (Shanghai, China). potassium chloride(KCl), sodium chloride(NaCl), ascorbic acid (AA), uric acid (UA), ethanol, sucrose (Suc), fructose (Fru), lactose (Lac) were purchased from China Pharmaceutical Group Chemical Reagent Company. Glucose (Glu), and Urea were purchased from Chongqing Chuan Dong Chemical Group (China). All chemicals used in these experiments were of standard analytical grade. Huangshui was obtained from Wuliangye Yibin Co., Ltd. (Sichuan, China). Deionized (DI) water was produced from a Milli-Q system (18.25 MΩ cm^{-1}).

The morphology characterization was tested by field-emission scanning electron

microscope (FESEM, JEOL-6300F) and Transmission electron microscopy (TEM, FEI Tecnai G2 F30). The crystal structures of the materials were characterized by powder X-ray diffraction (XRD, Maxima-X XRD-7000). Raman spectra of materials were recorded by Raman spectrometer (inVia, Renishaw Instrument Co., Britain). The chemical compositions were examined by an XPS spectrometer (ESCALAB 250Xi, ThermoFisher). The specific surface area and porosity of the samples were characterized by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods (Micromeritics, GA, USA)).

S2. Electrochemical measurement

Electrochemical tests including cyclic voltammetry (CV), Amperometric i-t curves were performed on a CHI 760E electrochemical workstation (Shanghai CH Instrument, China). The Pt and Ag/AgCl worked as counter electrodes and reference electrodes, respectively. The modified glass carbon electrode (GCE) was used as the working electrode. CV measurements between 0 V and 0.7 V at a scan rate of 50 mV s^{-1} were performed. The amperometric i-t was performed at 0.6 V. A solution of 0.1M NaOH was employed for the supporting electrolyte for glucose determination.

S3. Electrochemical Characterization

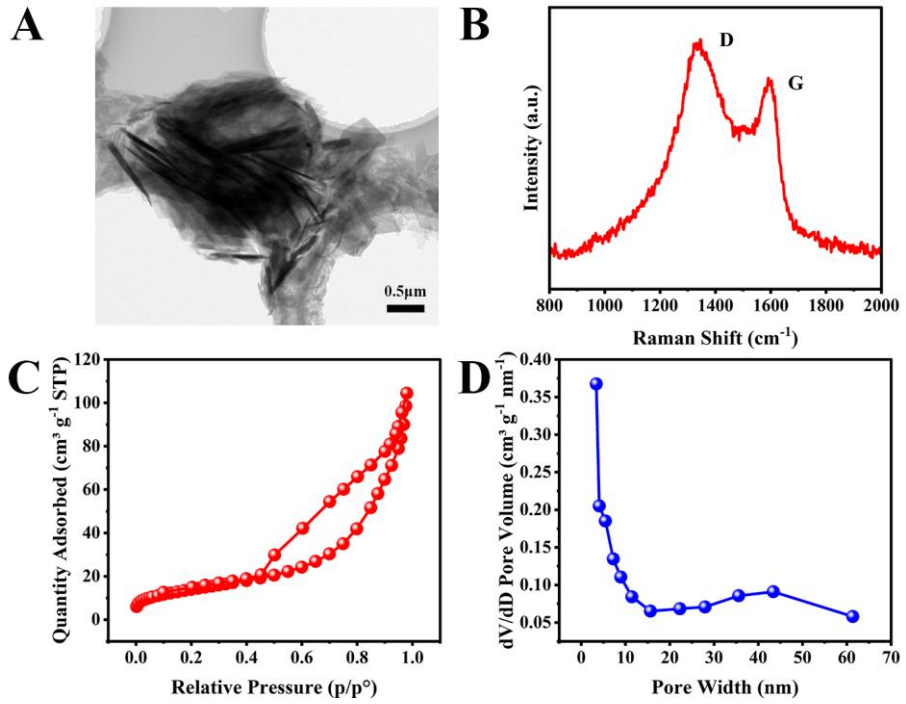

Fig. S1. (A) TEM images of NiCo-MOF/GO (B) Raman spectra of NiCo-MOF/GO (C) Nitrogen adsorption-desorption isotherms and (D) the pore size distribution of NiCo-MOF/GO

S4. Electrochemical Characterization

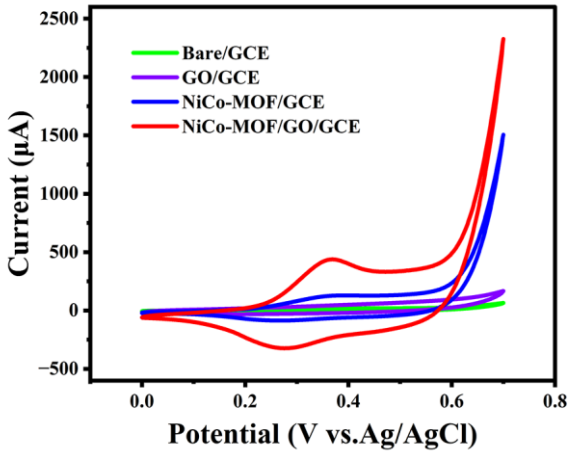

Fig. S2. CV curves of bare GCE, GO/GCE, NiCo-MOF/GCE, and NiCo-MOF/GO/GCE in 0.1 M NaOH. (scan rate: 50 mV s^{-1})

S5. Optimization of Detection Parameters

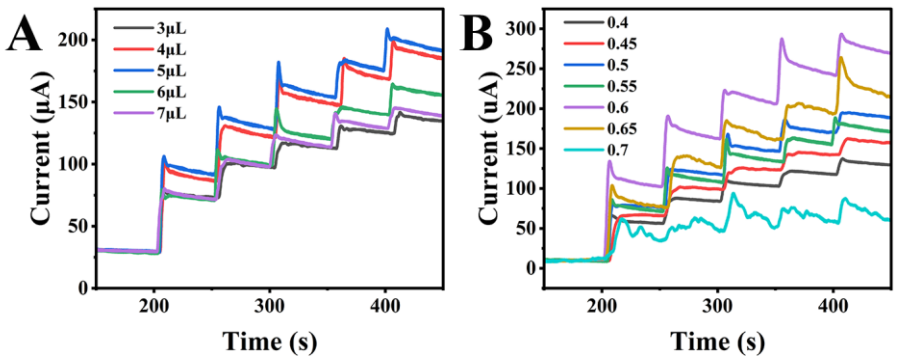

Fig. S3. Effect of (A) NiCo-MOF/GO loading volume and (B) applied potential on current response.

Table S1. Comparison of the proposed sensor with other electrochemical sensors for glucose determination.

Electrode material	Linear range (μM)	LOD (μM)	Ref.
Ni-MIL-77	1-500	0.25	[1]
Ni-MOF	10-2000	1.16	[2]
Co^{II}-MOF/Acb-2%	5-1000	1.7	[3]
Ag@ZIF-67	2-1000	0.66	[4]
Cu-in-ZIF-8	0-700	2.76	[5]
NiCo-MOF/GO	1-499,499-3997	0.23	This work

Reference

1. X. Xiao, S. Zheng, X. Li, G. Zhang, X. Guo, H. Xue and H. Pang, *Journal of Materials Chemistry B*, 2017, **5**, 5234-5239.
2. X. Xuan, M. Qian, L. Pan, T. Lu, L. Han, H. Yu, L. Wan, Y. Niu and S. Gong, *Journal of Materials Chemistry B*, 2020, **8**, 9094-9109.
3. Y. Wen, W. Meng, C. Li, L. Dai, Z. He, L. Wang, M. Li and J. Zhu, *Dalton Transactions*, 2018, **47**, 3872-3879.
4. W. Meng, Y. Wen, L. Dai, Z. He and L. Wang, *Sensors and Actuators B: Chemical*, 2018, **260**, 852-860.
5. L. Shi, X. Zhu, T. Liu, H. Zhao and M. Lan, *Sensors and Actuators B: Chemical*, 2016, **227**, 583-590.