Supporting Information

High-Performance Non-Enzymatic Biofuel Cells Based on Organic Copper Complex Cathode and Nanoporous Gold Nanoparticles Anode

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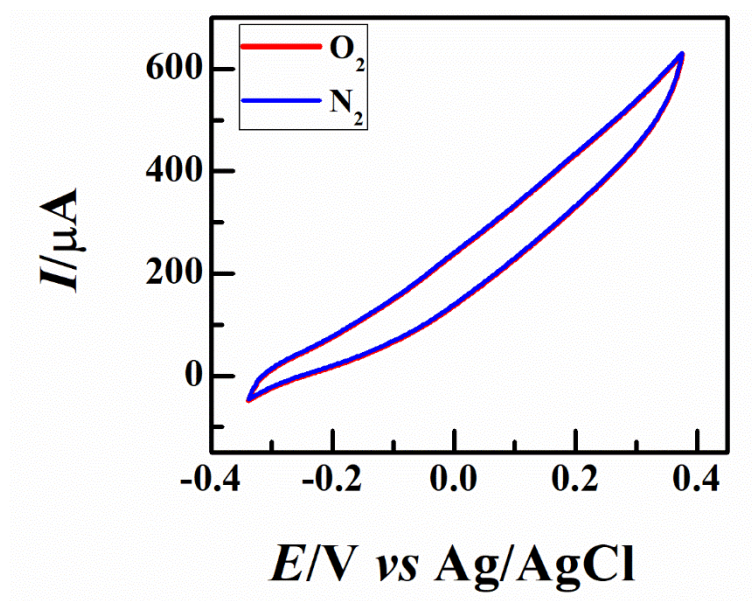
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Fig. S1 CVs of NPG modified anode in 0.1 M PB (pH 7.4) with glucose in N_2-saturated (a) and O_2-saturated (b) conditions.
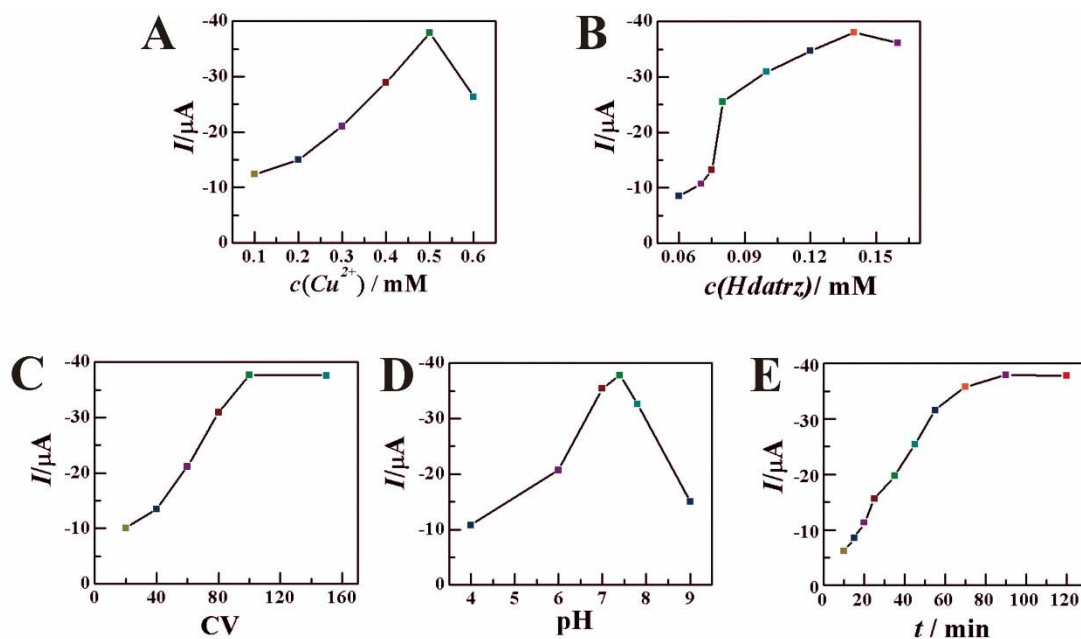
Fig. S2 (A) The relationship between the cathodic current and the different Cu^{2+} concentration (B) The relationship between the cathodic current and the different concentration of Hdatrz (C) The relationship between the cathodic current and the different number of CV circulation for the electroreduction of Hdatrz. (D) The relationship between the cathodic current and the different pH. (E) The relationship between the cathodic current and the different coordination time for Cu^{2+} with Hdatrz. The electrolyte solution was 0.1 M PB (pH=7.4) saturated with N_2.

As the above described, the O_2 reduction performance was mainly origin from the electrocatalytic activity of [Cu (Hdatrz)] complex. Therefore, a series of CVs were performed to explore the Cu^{II}/Cu^{I} redox peak for [Cu (Hdatrz)] complex under different conditions. As shown in Figure S2A, the amount of Cu^{2+} would directly affect the electrocatalytic activity. The Hdatrz modified ITO electrode would continually capture free Cu^{2+} until saturation. And the maximum redox peak was achieved at the Cu^{2+} concentration of 0.5 mM. However, the excessive Cu^{2+} would increase the amount of Cu^{II}-complex intermediate, thus a drop of redox peak for [Cu (Hdatrz)] complex itself could be observed. Therefore, 0.5 mM Cu^{2+} was used for the complexation with Hdatrz in this work. Figure S2B showed the effects of Hdatrz with different concentration on the electrocatalytic activity. The redox peak current increased quickly as the Hdatrz concentration varied from 0.08 to 0.12 mM, and presented a slight increase when the concentration of Hdatrz gradually reached the saturated state, thus 0.16 mM Hdatrz was used as the optimal condition.

Furthermore, different number of CV circulation for the electrografted Hdatrz played a crucial role in the stability of the catalytic performance. As shown in Figure S2C, initially, the redox peak current enhanced with the increase of CV circulation, because Hdatrz was gradually electrografted onto the surface of ITO electrode. When the number of CV circulation exceeded 100, the redox peak current remained unchanged, suggesting that the electrode surface has been occupied completely by Hdatrz. In order to ensure the optimal effect, 100 of CV circulation was chosen for this experiment. Certainly, the pH value of Cu^{2+} solution was another factor for the complexation between Cu^{2+} and Hdatrz. As indicated from Figure S2D, the maximum redox peak current appeared at pH 7.4, same as the physiological solution. Notably, an obvious decline of the current was observed when the pH changed from 8 to 9. The reason might be more $[OH^-]$ anions could significantly affect the $[Cu(Hdatrz)]$ complex. Hence, pH 7.4 was used as the optimal pH of Cu^{2+} solution during the process of soaking. In addition, Figure S1E illustrated the effects of different soaking times on redox peak current of Cu^{II}/Cu^{I}. The current reached a plateau at 90 min, indicating a complete complexation between Cu^{2+} and Hdatrz. So, 90 min was used as the optimal soaking time.
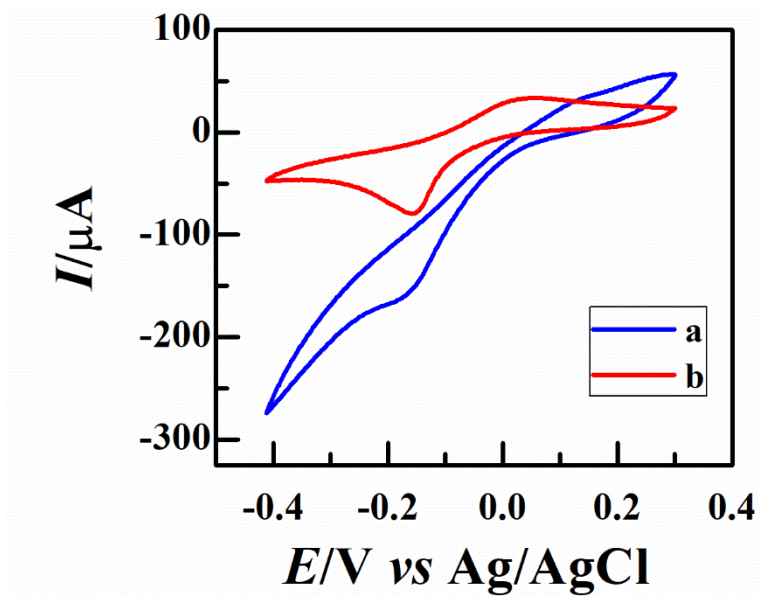
Fig. S3 Cyclic voltammetry analysis of the cathode in 0.10 M PB (pH 7.4) within O_2-saturated conditions in the absence (a) and presence of PPi (b).
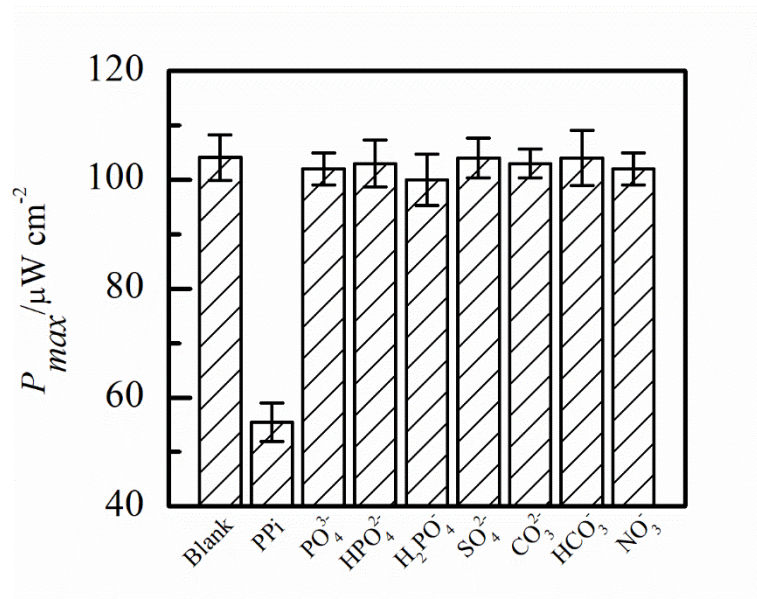
Fig. S4. P_{max} of the as-proposed biosensor for various anions at 0.1 nM concentration

Table S1 Comparison of the performance of NEFC by our method and those reported in literatures

Anodic material	Cathodic material	E^{OCV} (V)	P_{max} ($\mu W\ cm^{-2}$)	Electrolyte	Ref.
MWCNT/(DPDE)Rh(III)	MWCNT/phthalocyanincobalt(II)	0.64	0.18	0.5 M KOH	1
Nickeloxide-decorated graphene nanosheet (NiO/GNS)	Pt/C	0.75	No studied	0.1 M KOH	2
Nitrogen-doped graphene decorating Co nanoparticle hybrids (Co/NG)	Nitrogen-doped graphene decorating Co nanoparticle hybrids (Co/NG)	0.79	150.00	0.1 M KOH	3
Sn:Co$_3$O$_4$	Pt/C	Not studied	30.0	0.1 M KOH	4
Raney-platinum film	Raney-platinum film	0.50	4.40	PBS	5
Au nanowire (AuNW)	N-doped mesoporous carbon (N-m-C)	0.52	64.30	pH 7.4 PBS	6
Porous palladium	Porous palladium	0.65	5.70	pH 7.4 0.1 M PBS	7
NPG	[Cu (Hdatrz)]	0.81	104	pH 7.4 0.1 M PB	This work

Table S2. Comparison of analytical performance for PPi assay by our method and those reported in literature

Method	Strategy	LOD(M)	Dynamic range(M)	Ref.
Fluorescence	DNA scaffolded silver nanoclusters	1.1×10^{-7}	0.2×10^{-6}-1.0×10^{-4}	8
UV−vis spectrum	competitive coordination chemistry	2.4×10^{-5}	1.3×10^{-7}-1.3×10^{-3}	9
Fluorescent	Conjugated Polymers	1.0×10^{-6}	5.0×10^{-6}-2.4×10^{-5}	10
Near-IR Fluorescence	Gold nanorod @SiO$_2$@ meso-tetra(4-carboxyphenyl) porphyrin (TCPP)	8.2×10^{-7}	5.0×10^{-6}-7.5×10^{-5}	11
Fluorescence	single-stranded-DNA-Al(III) complex system	4.0×10^{-8}	4.0×10^{-8}-4.0×10^{-5}	12
Self-powered biosensor	NEFC	2.0×10^{-12}	1.0×10^{-11}-1.0×10^{-8}	This Work

References

1. K. Elouarzaki, G. A. Le, M. Holzinger, J. Thery and S. Cosnier, *J. Am. Chem. Soc.,* 2012, **134**, 14078-14085.

2. G. Zeng, W. Li, S. Ci, J. Jia and Z. Wen, *Sci. Rep*., 2016, **6**, 36454.

3. S. Ci, Z. Wen, S. Mao, Y. Hou, S. Cui, Z. He and J. Chen, *Chem. Commun.*, 2015, **51**, 9354-9357.

4. M. Chowdhury, C. Ossinga, F. Cummings, J. Chamier and M. Kebede, *Electroanalysis*, 2017, **27**, 1-12.

5. S. Kerzenmacher, U. Kräling, T. Metz, R. Zengerle and F. V. Stetten, *J. Power Sources*, 2011, **196**, 1264-1272.

6. M. Chu, Y. Zhang, L. Yang, Y. Tan, W. Deng, M. Ma, X. Su, Q. Xie and S. Yao, *Energy Environ. Sci.*, 2013, **6**, 3600-3604.

7. Z. Yue, L. Z. Fan, H. Bo, Z. Yang, M. S. Zhang, Q. M. Que and J. Y. Ji, *Energy Technol.*, 2016, **4**, 249-255.

8. J. L. Ma, B. C. Yin, X. Wu and B. C. Ye, *Anal. Chem.,* 2016, **88**, 9219-9225.

9. J. Deng, P. Yu, L. Yang and L. Mao, *Anal. Chem.*, 2013, **85**, 2516-2522.

10. Y. Bao, H. Wang, Q. Li, B. Liu, Q. Li, W. Bai, B. Jin and R. Bai, *Macromolecules.*, 2012, **45**, 3394-3401.

11. L. Wang, Q. Song, Q. Liu, D. He and J. Ouyang, *Adv. Funct. Mater.*, 2015, **25**, 7017-7027.

12. X. Su, C. Zhang, X. Xiao, A. Xu, Z. Xu and M. Zhao, *Chem. Commun.*, 2013, **49**, 798-800.