Supporting Information

In-situ Electrodeposition of FeCo-MOF on Au Ultramicroelectrode for Highly Sensitive Detection of Epinephrine

Yan Chen[a,b,1], Jian Shang[c,1], Siyu Wan[a,b], Xiaotong Cui[a,b], Zhonggang Liu[a,b,*], Zheng Guo[a,b,*]

[1]These authors contributed equally to this work.

Table of Contents

1. Experimental Procedures

Fabrication of a gold UME

Prior to the fabrication process, a borosilicate glass capillary (outer diameter: 1 mm, inner diameter: 0.2 mm) was ultrasonically cleaned with ethanol and acetone for 20 min each to ensure the removal of contaminants. Subsequently, the capillary was dried at 60ºC for 48 h. A gold wire (diameter: 10 μm) with a length of approximately 1.5 cm was carefully inserted into the center of the borosilicate glass capillary. The gold disk UME was conducted using a P-2000 pipette puller (P-2000, Sutter Instrument Co., CA) in a four-step process. The first two steps included the pre-thin of the borosilicate glass capillary and the sealing of the gold wire. The sealing process was programmed to repeat four times with each cycle lasting approximately 5 s and a cooling interval of 40 s. To maintain a vacuum state with the glass capillary and prevent bubble formation during the high-temperature sealing process, both ends of the capillary were connected to a vacuum pump. Additionally, to prevent any movement of the glass capillary during the sealing process, two customized clamps were affixed the puller rods at both ends of the laser puller. In the third step, the borosilicate capillary was puller to from two symmetrical and sharped tips. subsequently, a copper wire was stick to the gold wire with silver epoxy, which was then dried at 120ºC for 3 h. The final step involved a gentle polishing of the fabricated gold disk UME using alumina polishing powders to expose gold with a smooth, crack-free cross-section (Fig. S1). The size of the gold disk UME was calculated based on the diffusion-limited steady-state current in a FcMeOH ethanol aqueous solution (Fig. S2).

2. Au UME Characterization.

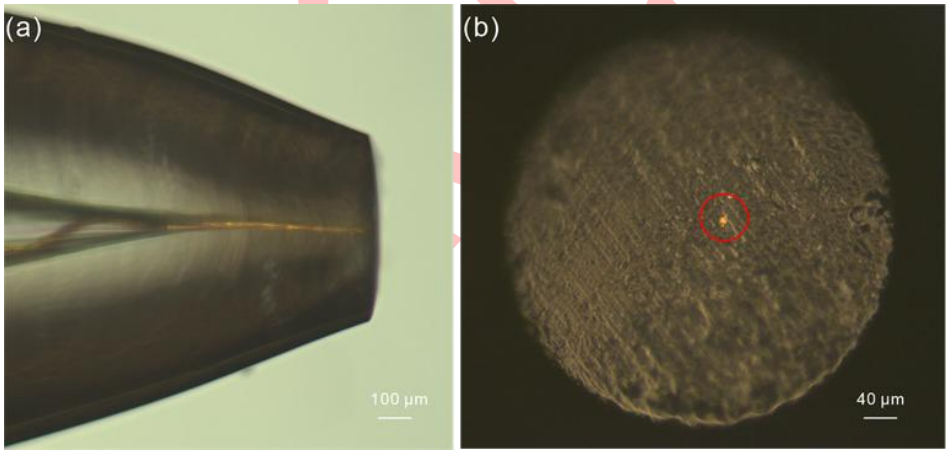

Fig. S1. Optical photographs of the fabricated Au UME with a diameter of 5.0 μm. (a) Side view and (b) Top view.

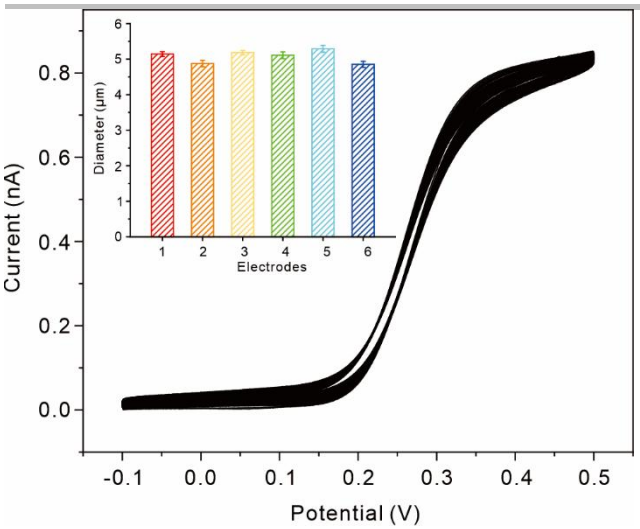

Fig. S2. CV curves of Au UMEs in 0.1 M KCl solution containing 1.0 mM FcMeOH. Inset shows the calculated diameters of Au UMEs fabricated in different batches. Error bars correspond to the standard deviation of three independent measurements.

The electrochemical characteristics of the Au disk UME was tested using CV with FcMeOH as the redox probe. As shown in Fig. S2, the Au disk UMEs fabricated in different batches exhibit the steady-state CV curves with typical S-shape, indicating the ultramicroelectrode characteristics with good reproducibility. The radius (a) of the Au UME is measured by the steady-state current (I_{ss}) based on the following equation:

$$I_{ss} = 4nFDC^{*}a$$

where I_{ss} is the stable-state current, n is the number of electrons, F is Faraday's constant (96485 C mol^{-1}), D is the diffusion coefficient (7.8 × 10^{-6} cm^2 s^{-1} for FcMeOH), and C is the concentration of the redox probe (1.0 mM FcMeOH). The radius was calculated to be 2.6 μm.

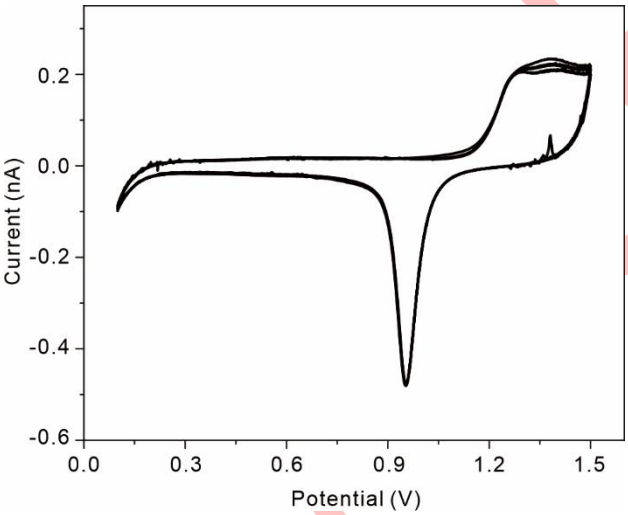

Fig. S3. Cyclic voltammogram recorded at the gold ultramicroelectrode in 0.1 M H2SO4 solution. Scan rate: 50 mV s^{-1}.

3. EDS of FeCo-MOF/Au UME

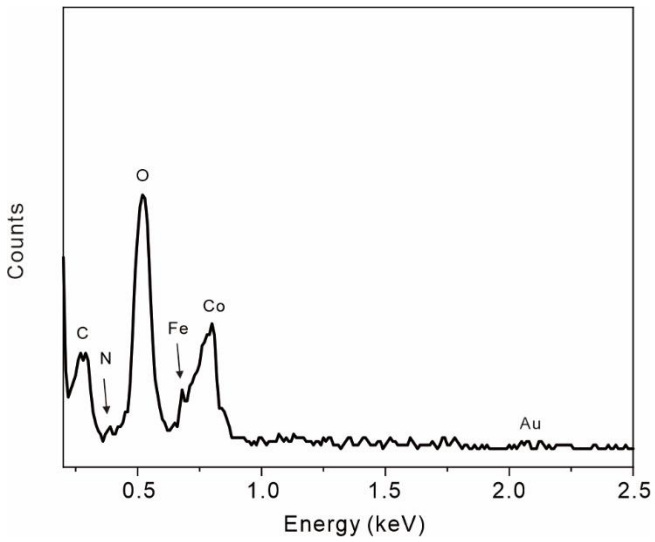

Fig. S4. EDS spectrum of FeCo-MOF/Au UME.

4. Electrochemical Sensing of EP at Au UME

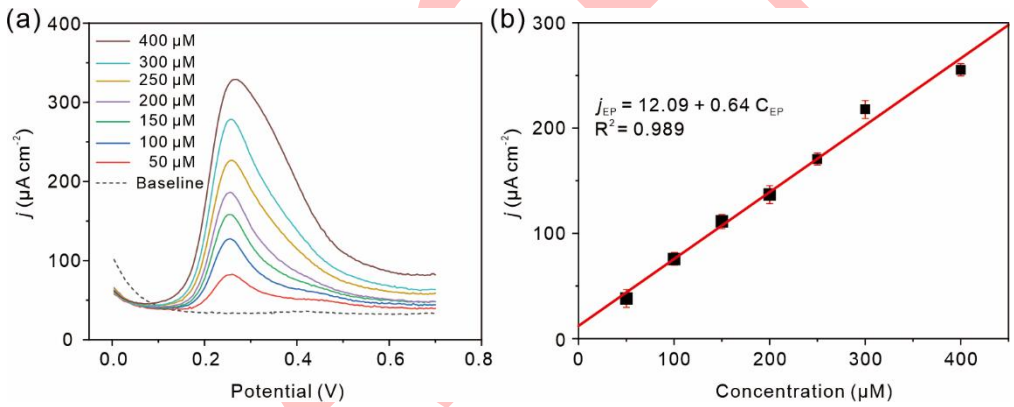

Fig. S5. (a) The current densities of Au UME on analyzing EP in different concentrations ranged from 50 μM to 400 μM in 0.1 M PBS solution (pH 7.4). (b) The corresponding calibration plot between the current densities and the concentrations.

5. Electrochemical Sensing of EP at Fe-MOF/Au UME and Co-MOF/Au UME

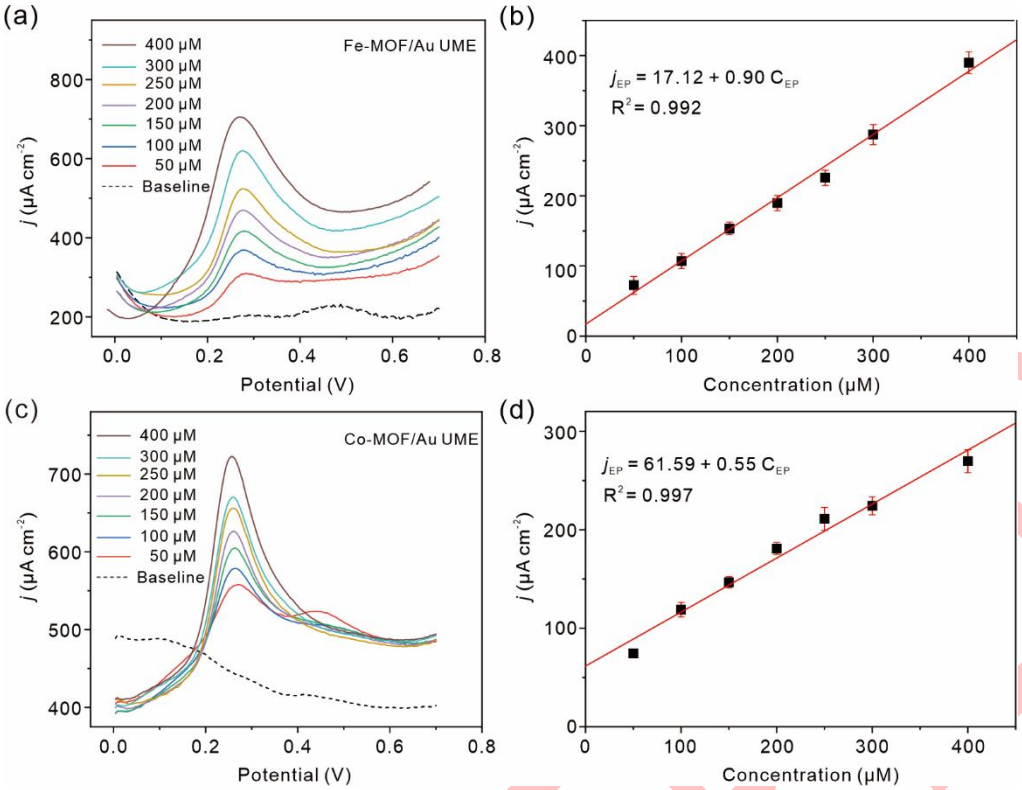

Fig. S6. The current densities of (a) Fe-MOF/Au UME and (c) Co-MOF/Au UME on analyzing EP in different concentrations ranged from 50 μM to 400 μM in 0.1 M PBS solution (pH 7.4). (b, d) The corresponding calibration plots between the current densities and the concentrations.

6. Real Sample Analysis

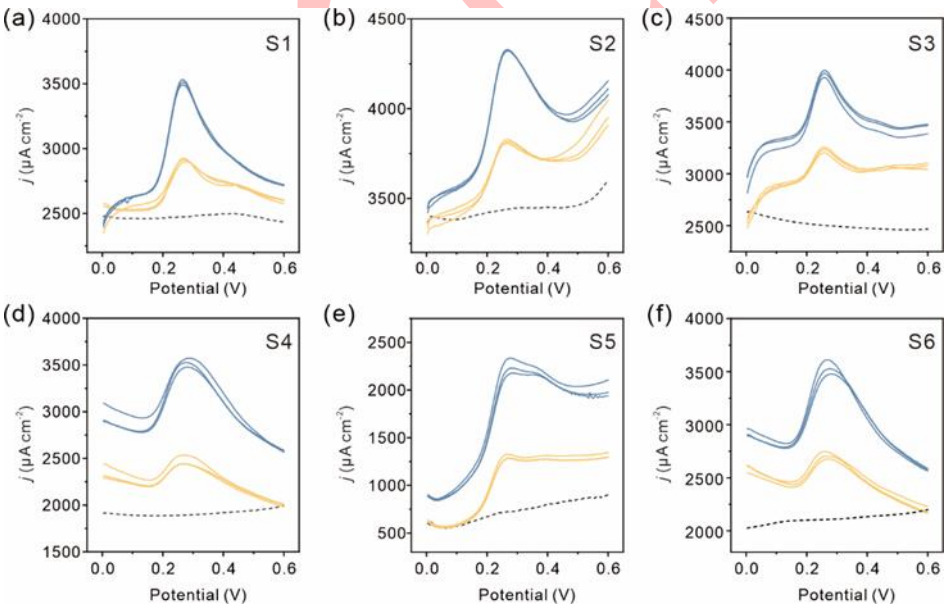

Fig. S7. (a-f) SWV curves of FeCo-MOF/Au UME on detecting of 20 μM and 50 μM EP in different human serum samples.

7. Electrochemical Sensor Performance Comparison

Table S1. A comparison of electrochemical performance of the electrochemical sensors for the detection of EP.

Electrodes	Linear range (μM)	Sensitivity (μA μM^{-1} cm^{-2})	LOD (μM)	Refs.
NP Au film	20 – 190	1.13	2.43	[1]
Au/MPTMS/ITO	5 – 2000	-	1.8	[2]
h-nPG/Au microneedles	0 – 850	2.4	0.1	[3]
ZIF-67/GCE	0 – 50	0.06	2.1	[4]
MWCNT/CAP/GCE	50 – 1150	3	7.2	[5]
MWCNT/Fe_3O_4/2,3-Nc/GCE	7.5 – 48	0.214	12.3	[6]
MWCNT/GCE	22.5 – 547	0.0687	3.92	[7]
Nanostructured Au electrode	60 – 1000	0.22	7.3	[8]
SPCE/CB-ERGO	10 – 100	1.44	1.8	[9]
Au-Ag film	10 – 275	1.52	5.05	[10]
FeCo-MOF/Au UME	20 – 300	36.93	1.28	This work

References

[1] Wierzbicka E, Sulka G D. Fabrication of highly ordered nanoporous thin Au films and their application for electrochemical determination of epinephrine[J]. Sens. Actuators B: Chem., 2016, 222: 270-279.

[2] Zhang J D, Kambayashi M, Oyama M. Seed mediated growth of gold nanoparticles on indium tin oxide electrodes: Electrochemical characterization and evaluation[J]. Electroanalysis, 2005, 17 (5-6): 408-416.

[3] Tortolini C, Cass A E G, Pofi R, Lenzi A, Antiochia R. Microneedle-based nanoporous gold electrochemical sensor for real-time catecholamine detection[J]. Microchim. Acta, 2022, 189 (5): 180.

[4] Soosaimanickam C, Sakthivel, A, Murugavel, K, Alwarappan, S. Zeolite imidazolate framework-based platform for the electrochemical detection of epinephrine[J]. J. Electrochem. Soc., 2023, 170 (10): 107504.

[5] Da Silva L V, Dos Santos N D, De Almeida A K A, Dos Santos D D E R, Ferreira Santos A C, Franca M C, Lima D J P, Lima P R, Goulart M O F. A new electrochemical sensor based on oxidized capsaicin/multi-walled carbon nanotubes/glassy carbon electrode for the quantification of dopamine, epinephrine, and xanthurenic, ascorbic and uric acids[J]. J. Electroanal. Chem., 2021, 881: 114919.

[6] Mphuthi N G, Adekunle, A S, Ebenso E E. Electrocatalytic oxidation of Epinephrine and Norepinephrine at metal oxide doped phthalocyanine/MWCNT composite sensor[J]. Sci. Rep., 2016, 6: 26938.

[7] Tohidinia M, Noroozifar M. Investigation of carbon allotropes for simultaneous determination of ascorbic acid, epinephrine, uric acid, nitrite and xanthine[J]. Inter. J. Electrochem. Sci., 2018, 13 (3): 2310-2328.

[8] Wierzbicka E, Szultka Mlynska M, Buszewski B, Sulka G D. Epinephrine sensing at nanostructured Au electrode and determination its oxidative metabolism[J]. Sens. Actuators B: Chem., 2016, 237: 206-215.

[9] Ibanez Redin G, Wilson D, Goncalves D, Oliveira O N, Jr. Low-cost screen-printed electrodes based on electrochemically reduced graphene oxide-carbon black nanocomposites for dopamine, epinephrine and paracetamol detection[J]. J. Colloid Interface Sci., 2018, 515: 101-108.

[10] Wierzbicka E, Sulka G D. Nanoporous spongelike Au-Ag films for electrochemical epinephrine sensing[J]. J. Electroanal. Chem., 2016, 762: 43-50.

Author Contributions

Yan Chen: Investigation, Methodology, Data curation, Writing - original draft, **Jian Shang:** Methodology, Data curation, Writing - original draft. **Siyu Wan:** Formal analysis, Writing - original draft. **Xiaotong Cui:** Writing-review & editing. **Zhonggang Liu:** Investigation, Methodology, Writing-review & editing, Supervision. **Zheng Guo:** Methodology, Writing - original draft, Formal analysis, Supervision.