

Supplementary Information

Metal-Organic Framework Biosensor with High Stability and Selectivity in the Bio-mimic Environment

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1. Experimental Part

1.1 Chemicals and Instrumentation

Copper(II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), 2,5-dicarboxylic acid-3,4-ethylene dioxythiophene (H_2L , >95%), N,N-dimethylacetamide (DMA, >99%), L(+)-ascorbic acid (AA, >99%) and all the amino acids were purchased from commercial suppliers (Aladdin-reagent and TCL-reagent) and were used as received without further purification. All solutions were prepared with ultrapure water.

The phases were analyzed by X-ray powder diffraction (XRD) using a D/Max-2500 X-ray diffractometer with Cu $K\alpha$ radiation. The FT-IR spectra were measured with a Bruker Tensor 27 spectrophotometer on KBr disks. TGA experiment were performed on a NETZSCH TG 209 instrument with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The morphologies were examined by a high-resolution TEM (FEI, Tecnai G2F20, USA) microscopes.

1.2 Synthesis of $\{[\text{Cu}_2(\text{H}_2\text{L})_2(\mu_2\text{-O})_2(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}\}_n$ (**1**)

A mixture of 34.10 mg (0.2 mmol) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 46.04 mg (0.2 mmol) H_2L was dissolved in a mixture of 5 mL DMA and 10 mL H_2O , and then heated for 2 days at $90\text{ }^\circ\text{C}$ in a Parr Teflon-lined stainless steel vessel (23 mL), then cooled to room temperature slowly in 2 days. Green diamond-like crystals of **1** were collected at the bottom of the glass vessel. Yield: 50.2 mg (69.1 %). Anal. Calc for $\text{C}_{16}\text{H}_{22}\text{Cu}_2\text{O}_{20}\text{S}_2$: C, 26.42; H, 3.32 Found: C, 27.42; H, 4.00 (%); IR (KBr disk/ cm^{-1}) 3323.66 m, 2961.15 m, 1603.28 s, 1451.22 m, 1387.15 s, 1350.26 s, 1200.57 w, 1100.17 s, 848.01 w, 793.57 w, 734.69 w, 538.48 w.

1.3 Electrochemical Section

Cyclic Voltammetry (CV) Analysis: An Epsilon electrochemical workstation (made in USA) was used for CV studies. Three-electrode system was used as follow: the working electrode was **1**-GCE; the auxiliary electrode was a platinum wire, and the reference electrode was an Ag/AgCl (sat. KCl) electrode. All studies were carried out at room temperature and under nitrogen surroundings. For the pH measurements a pH meter with a combined glass electrode was used.

Ultra-pure water (ulup, 18.2 M Ω cm, 25 °C) was used to prepare all electrolyte solutions. For electrochemical measurements a K₂HPO₄/KH₂PO₄ buffer solution (pH = 6.8) was used, which was prepared by mixing suitable volumes of 0.2 mol·cm⁻³ K₂HPO₄ solution and 0.2 mol·cm⁻³ KH₂PO₄ solution.

Prior to be used, the glass carbon electrode (GCE) was carefully polished with an alumina slurry (0.5 μ m particle size) until a mirror-like surface was obtained, then rinsed ultrasonically with ultrapure water, nitric acid (1:1, v/v), sodium hydroxide (0.1 mol·cm⁻³) and ethanol, respectively, to remove any alumina residue from the electrode surface. The ultrasonic process was handled with an ultrasonic cleaning machine (Elma, S100H).

Electrode modification was performed as follow: depositing 0.020 g **1** dissolved in the gelatin (0.5 g, 10 mL H₂O), and 10 μ L of this solution were putting on the GCE surface. Then a clean beaker was coated on the modified electrode, which was dried in the air for 12 h.

Impedance Analysis: Electrochemical Impedance Spectroscopy (EIS) was performed using a Zahner-Zennium electrochemical workstation (made in Germany). All samples were collected using a three-electrode system (the working electrode was **1-GCE**; the auxiliary electrode was a platinum wire and the reference electrode was an Ag/AgCl (sat. KCl) electrode) in 10 mL 0.1 M KCl solution containing 5 mM potassium ferricyanide, which acted as an electrolyte (EIS frequency was cycled between 0.1 Hz – 100 kHz).

2. Characterization

2.1 X-ray crystallography

Diffraction intensity data for single crystals of **1** was collected on a Agilent Technologies SuperNova Single Crystal Diffractometer at 293 (2) K equipped with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques)¹ in the Olex2 package.²

Table S1. Crystal data and structure refinements for **1**

formula	C ₁₆ H ₂₄ Cu ₂ O _{19.5} S ₂
M, g mol ⁻¹	719.5741
cryst syst	Triclinic system
space group	<i>P</i> -1
<i>a</i> / Å	7.6226(6)
<i>b</i> / Å	8.0332(7)
<i>c</i> / Å	19.2709(16)
α / deg	89.772(7)
β / deg	88.902(7)
γ / deg	76.322(7)
<i>V</i> / Å ³	1146.35(17)
<i>Z</i>	2
reflns collected	7937
unique reflns	4037
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0684
<i>wR</i> 2(all data)	0.1947

One of the Cu centers is disordered to two positions (Cu1, Cu1') in **1**. The selected crystal parameters, data collection, and refinements are summarized in Table S1.

1. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

2.2 N₂ sorption isotherm of 1

The evaluated Brunauer-Emmett-Teller (S_{BET}) and Langmuir surface areas (S_{Langmuir}) from the N₂ adsorption isotherms are 88.1 and 116.8 m²/g for 1, respectively.

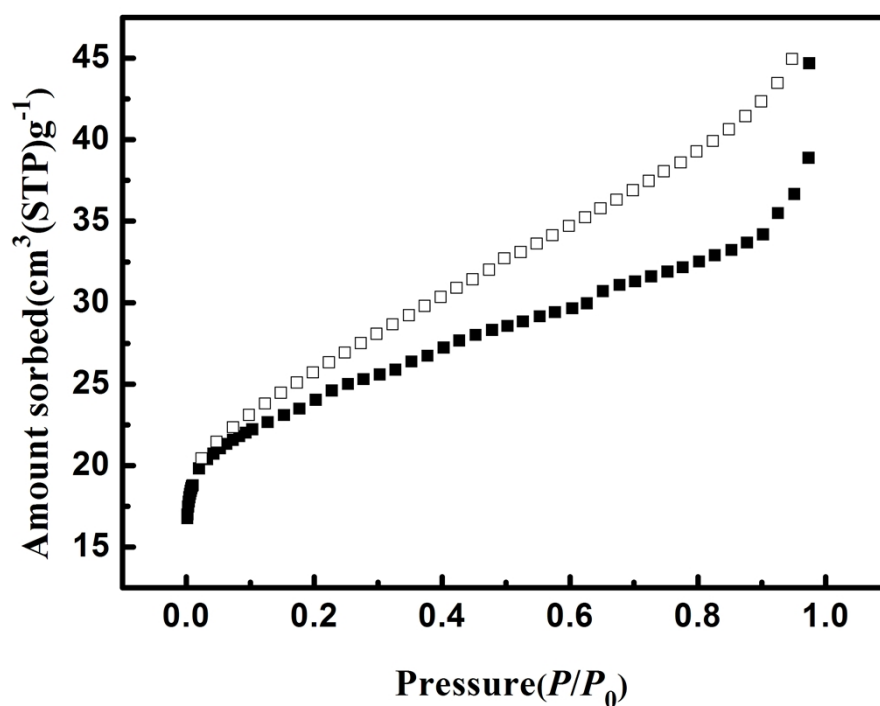


Fig. S1. N₂ sorption isotherm of 1 at 77 K (filled and open symbols represent adsorption and desorption data, respectively).

2.3 Thermal Gravimetric Analyses.

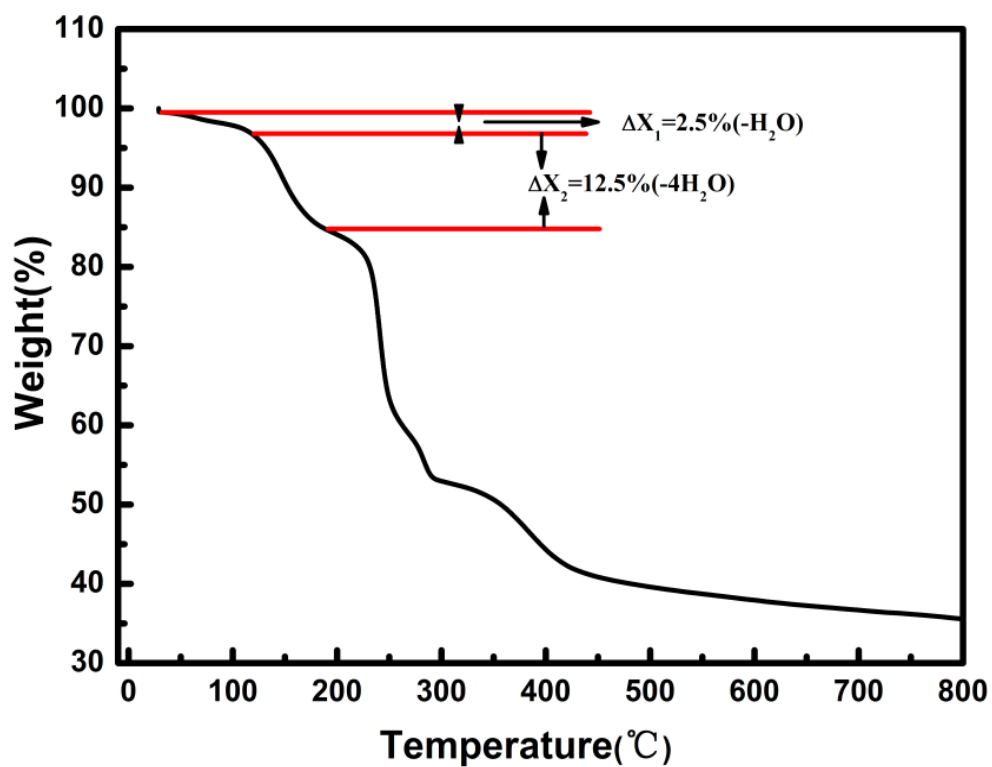


Fig. S2. Thermal gravimetric analyses (TGA) of 1

2.4 Powder X-ray Diffraction patterns.

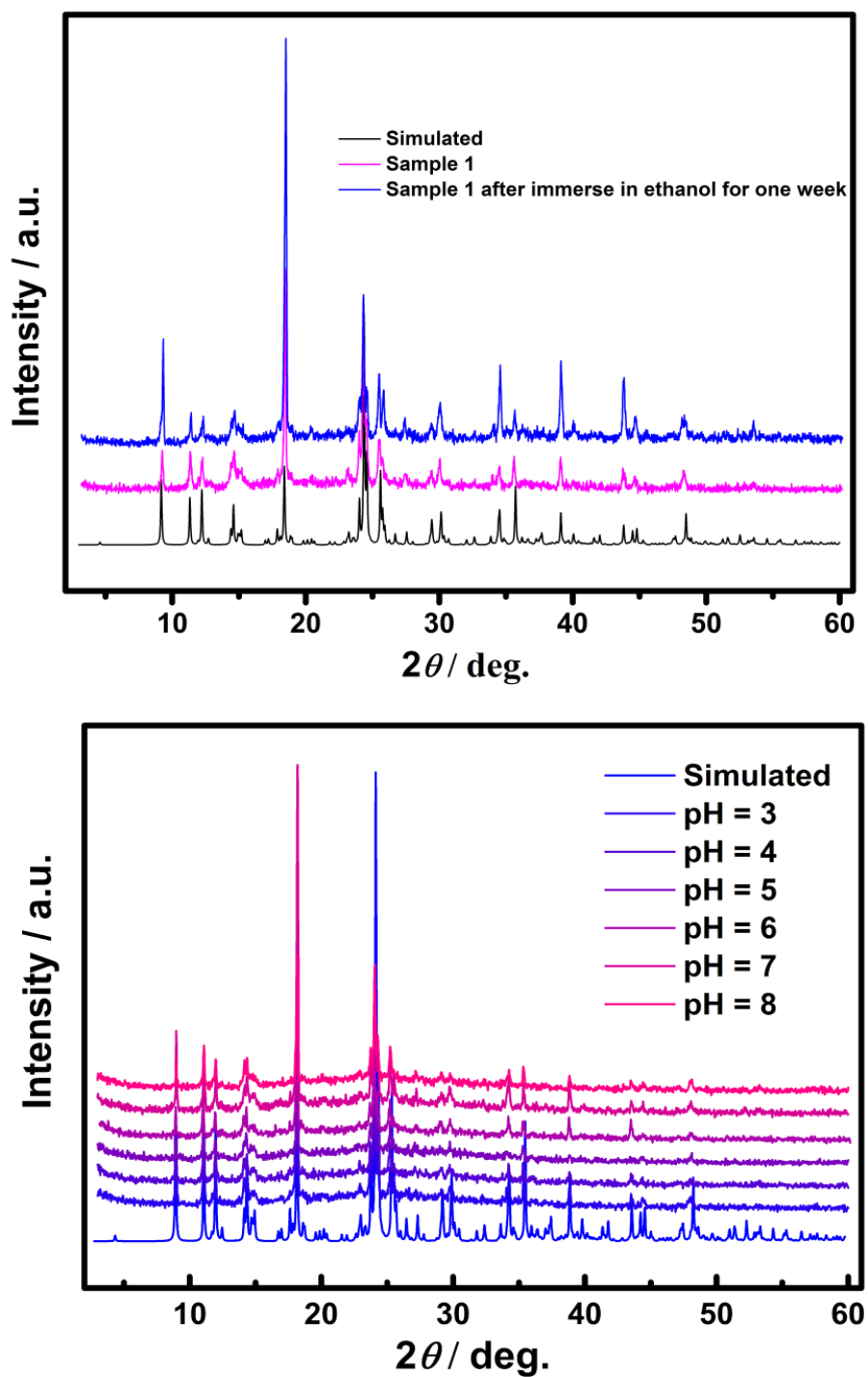


Fig. S3. Top: PXRD patterns of the simulated one of **1**, sample **1** and sample **1** after immersed in ethanol for one week. Bottom: PXRD patterns of **1** in different pH aqueous solution and the simulated one from single-crystal data.

3. Electrochemical Characterization

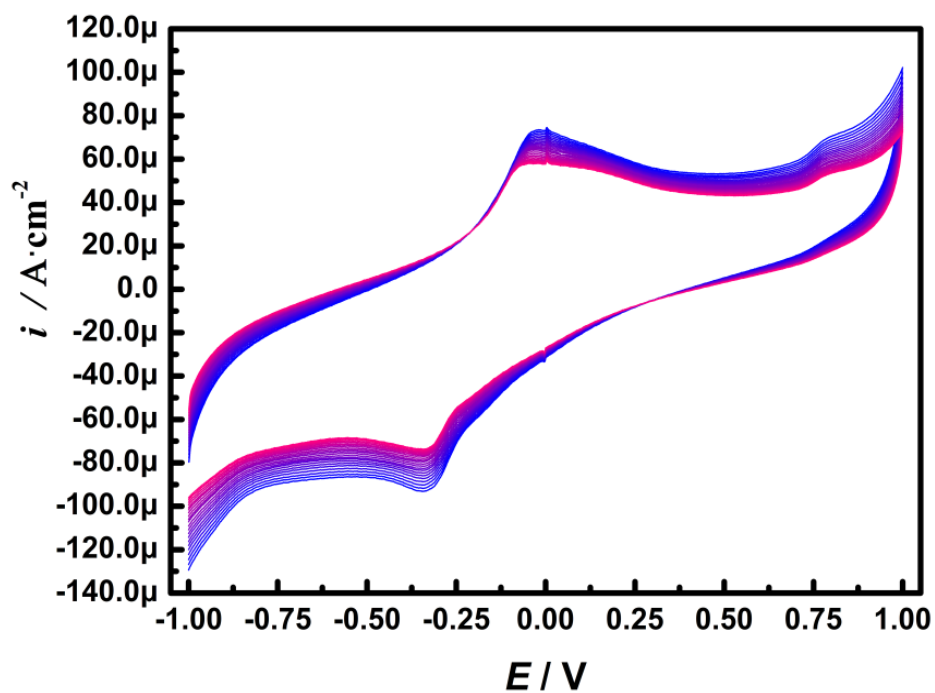


Fig. S4. Cyclic voltammetry in phosphate buffer solution (pH 6.8) at 1-GCE for 20 circles.

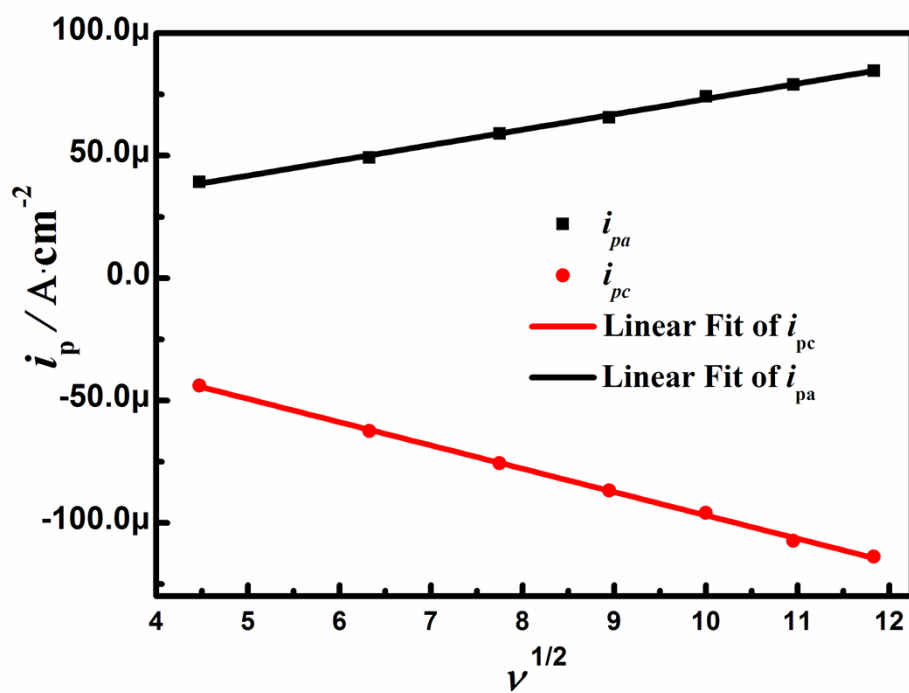


Fig. S5. Plots of i_{pa} and i_{pc} vs square root of scan rate $v^{1/2}$, respectively, for Fig. 2b.

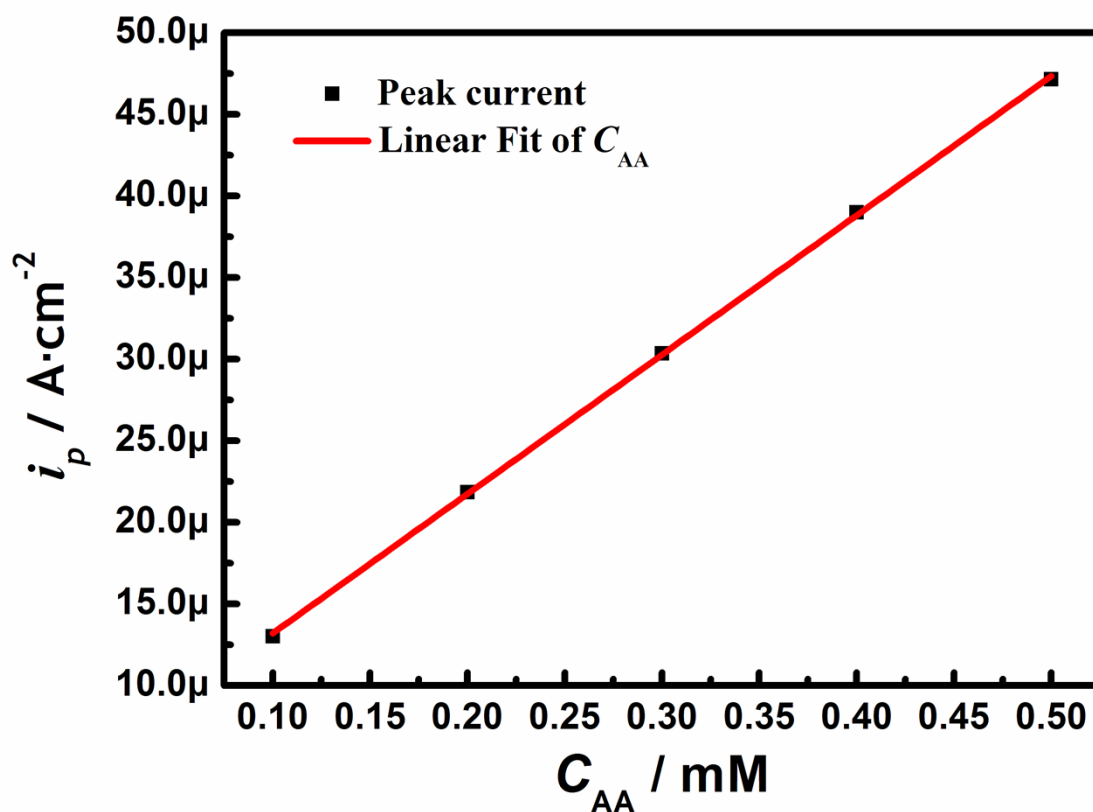


Fig. S6. Plots of i_{pa} vs AA concentration (C_{AA}) for Fig. 4a.

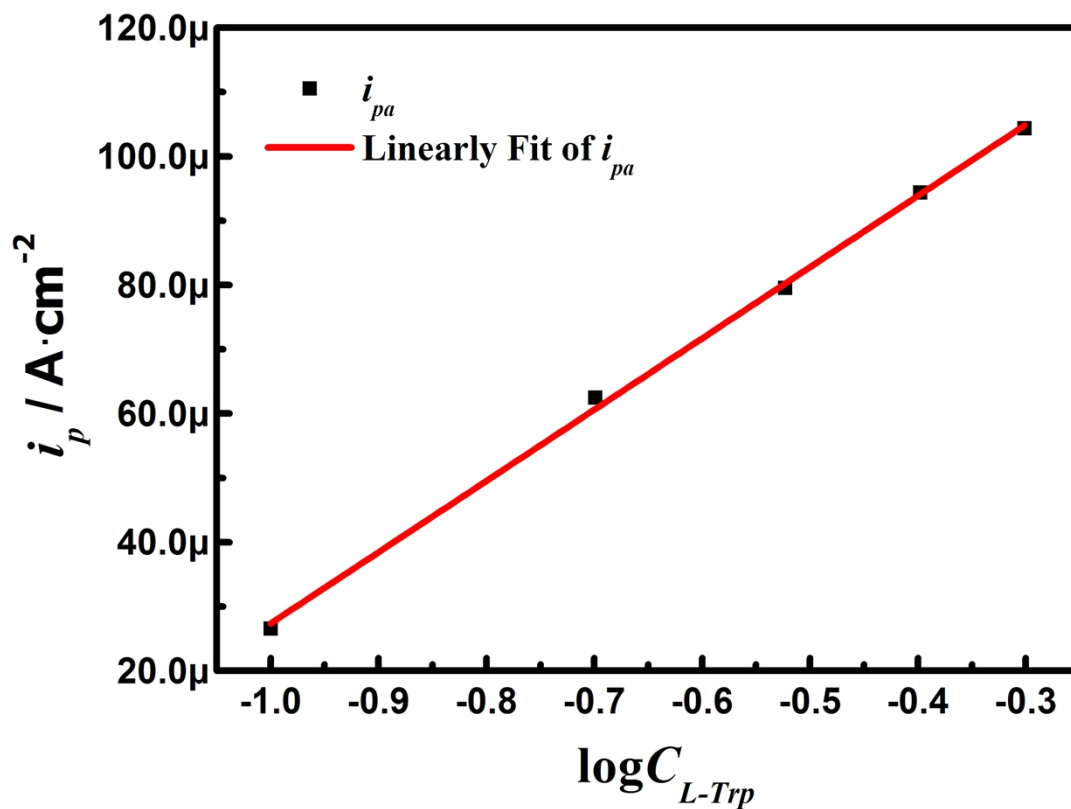


Fig. S7. Plots of i_{pa} vs L-Trp concentration for Fig. 4b.

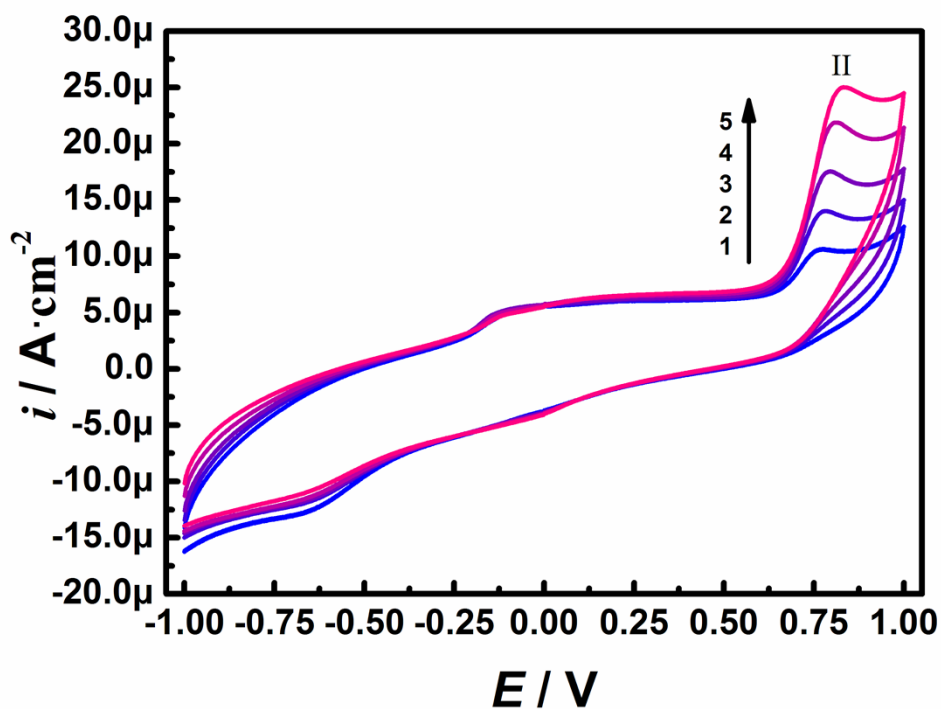


Fig. S8. Cyclic Voltammograms of 1-GCE in pH 6.8 buffer solution with the concentration of L-Trp: 0.1, 0.2, 0.3, 0.4 and 0.5 mM, respectively (scan rate 100 mv/s).

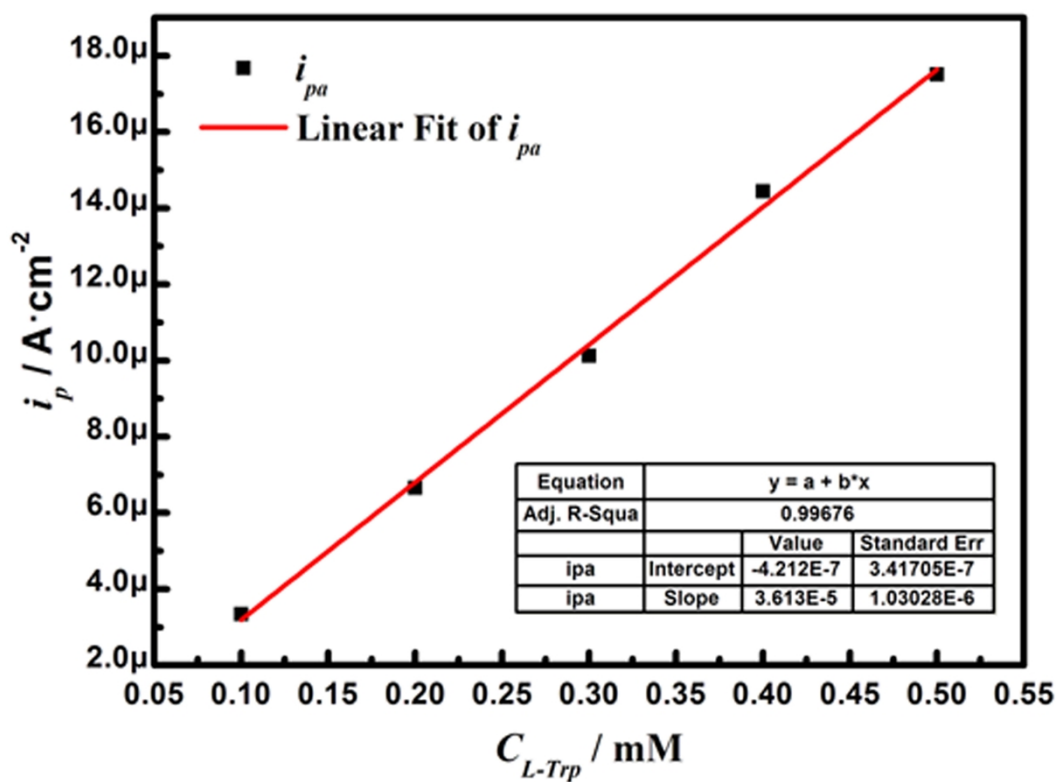


Fig. S9. Plots of i_{pa} vs. L-Trp concentration for Fig. S7.