

Electronic Supplementary Information

Integration of copper-based metal-organic framework with ionic liquid for electrochemically discriminating cysteine enantiomers

Qian-xiu Pan,^a Chen-yu Zhu,^b Jie Dong,^a Baogang Zhang,^{*a} Lin Cui,^{*b} Chun-yang Zhang^{*c}

^a College of Pharmacy, Department of Pathology, Weifang Medical University, Weifang 261053, China

^b College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, China.

^c School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China.

Email: Zhangbg@wfmc.edu.cn (B. Zhang); zpbzcl@126.com (L. Cui); zhangcy@seu.edu.cn (C.Y. Zhang).

3.1 Morphological characterization of Cu-MOF

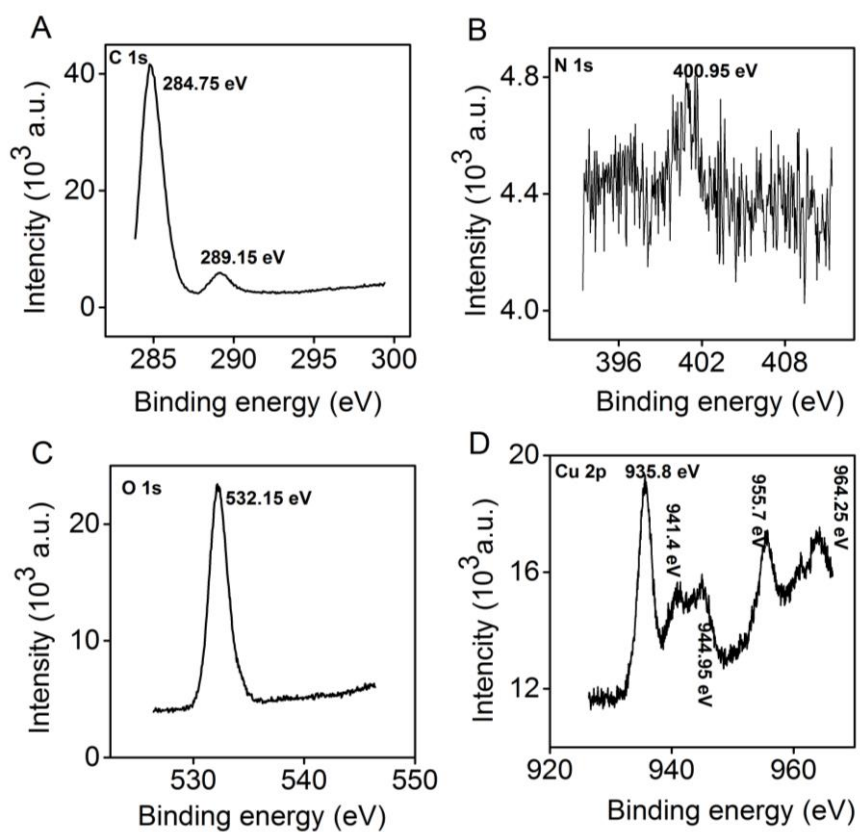


Fig. S1 XPS diagram of C 1s (A), N 1s (B), O 1s (C) and Cu 2p (D) in the Cu-MOF.

3.2 Optimization of experimental conditions

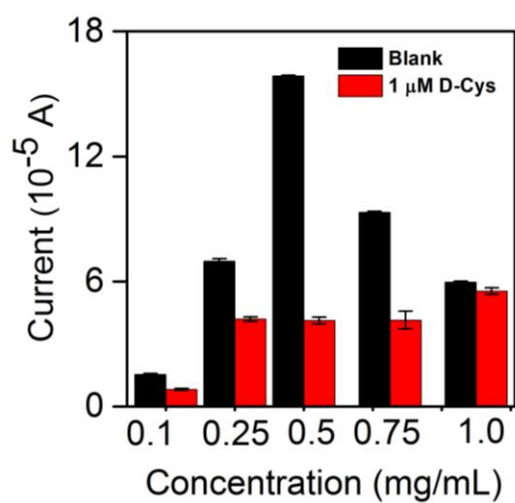


Fig. S2 Effect of the Cu-MOF concentration upon the cathode peak current of the Cu-MOF/GCE in PBS + ionic liquid without D-Cys (black column) and with $1 \mu\text{M}$ D-Cys (red column), respectively.

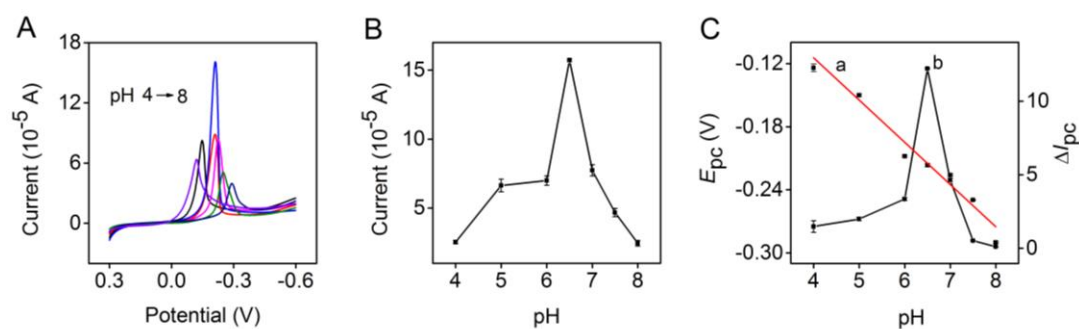


Fig. S3 (A) Cyclic voltammograms of the Cu-MOF/GCE in PBS in response to different pH: 4.0, 5.0, 6, 6.5, 7, 7.5 and 8.0. (B) Effect of pH upon the cathode peak current of the Cu-MOF/GCE in PBS. (C) Effect of pH upon (a) the cathode peak potential (E_{pc}) and (b) change of cathode peak current of the Cu-MOF/GCE without D-Cys (I_{blank}) and with D-Cys (I_{D-Cys}) in response to different pH. $\Delta I_{pc} = I_{blank} - I_{D-Cys}$.

We optimized the experimental conditions including the concentration of Cu-MOF and the pH of solution. As shown in Fig. S2, the change of peak current ($I_{Blank} - I_{D-Cys}$) enhances with the increasing concentration of the Cu-MOF from 0.1 to 0.5 mg/mL, followed by the decrease beyond the concentration of 0.5 mg/mL. This can be explained by that the low amounts of Cu-MOF cannot provide enough copper ions to participate the redox reaction when the concentration of Cu-MOF is less than 0.5 mg/mL, but the excess Cu-MOF may induce large resistance to prevent the electron transport, resulting in the decrease of peak current. Thus, 0.5 mg/mL Cu-MOF is used in subsequent researches.

We further investigated the influence of pH upon the cathode peak current (I_{pc}) and cathode peak potential (E_{pc}) of the Cu-MOF/GCE (Fig. S3), and examined the variance of cyclic voltammograms of Cu-MOF/GCE in PBS in response to different pH (Fig. S3A). The cathode peak current of Cu^{2+} enhances with pH from 4.0 to 6.5, followed by the decrease beyond the pH of

6.5 (Fig. S3B) due to the structural damage of the Cu-MOF induced by alkaline solution. Thus, pH 6.5 is used in subsequent researches. The isoelectric point of cysteine is 5.05, and thus D-Cys presents a basic state at the buffer pH value of 6.5. As a result, the -COOH of D-Cys will lose its proton to form -COO⁻, which can electrostatic interaction with Cu-MOF. The cathode peak potential (E_{pc}) migrates to the negative direction with the increasing pH, with a linear equation of $E_{pc} = -0.0402 \text{ pH} + 0.0465$ ($R^2 = 0.9436$) (Fig. S3C, curve a). The electrochemical signal of Cu-MOF is affected by pH, suggesting that the proton is directly involved in the electrochemical redox process of the Cu-MOF.

3.3. Effect of scan rate upon the electrochemical signal

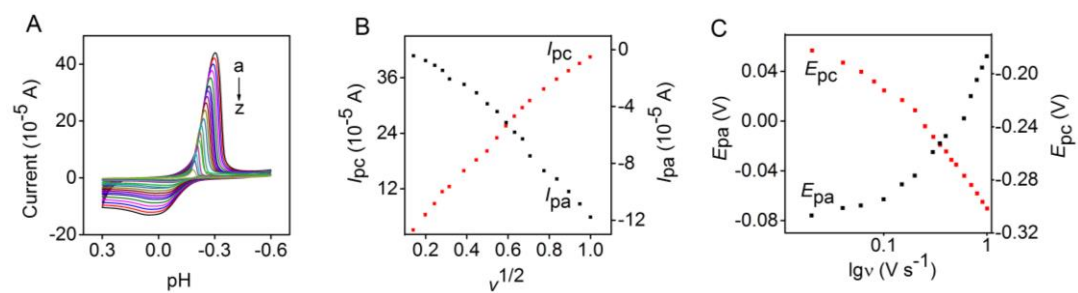


Fig. S4. (A) Cyclic voltammograms of Cu-MOF/GCE in 0.1 M PBS with ionic liquid at different scan rates from (a) to (z): 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.60, 0.70, 0.80, 0.90, and 1.0 V/s. (B) Relationship of anode (I_{pa} , black spot) and cathode peak current (I_{pc} , red spot) versus the square root of scan rate. (C) Relationship of anode (E_{pa} , black spot) and cathode (E_{pc} , red spot) peak potential versus the logarithm value of scan rate.