

## Supplementary Information

### **An electrochemiluminescence aptasensor based on highly luminescent silver-based MOF and biotin-streptavidin system for mercury ions detection**

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## Materials and Reagents

Silver nitrate ( $\text{AgNO}_3$ ), chloroauric acid ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ), sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) and methanol ( $\text{CH}_3 \cdot \text{OH}$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium borohydride ( $\text{NaBH}_4$ ), triethylamine (TEA), terephthalic acid ( $\text{H}_2\text{BDC}$ ), potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) and standard solution of mercury ions were acquired from Shanghai Macklin Biochemical Technology Co., Ltd (Shanghai, China). Tris(2-carboxyethyl) phosphine hydrochloride (TCEP), 6-mercaptohexanol (MCH), dibasic sodium phosphate ( $\text{Na}_2\text{HPO}_4$ ), Tris-EDTA (TE) buffer and streptavidin were acquired from Shanghai Sangon Biological Engineering Technology Co., Ltd (Shanghai, China). Sodium chloride ( $\text{NaCl}$ ) was purchased from Tianjin Da Mao Chemical Reagent Factory (Tianjin, China). Potassium hexacyanoferrate ( $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ ) was supplied by Guangfu Chemical Reagent Co., Ltd (Tianjin, China).

All of DNA sequences were purchased from Shanghai Sangon Biological Engineering Technology Co., Ltd (Shanghai, China).

cDNA: 5'-TAA GAA AGA GGG GAC AAA CAA-( $\text{CH}_3$ )<sub>6</sub>-SH-3'

Apt-Hg: 5'-TTG TTT GTC CCC TCT TTC TTA-Biotin-3'

## Apparatus

Scanning electron microscope (SEM; REGULUS8230, HITACHI, Japan), Transmission electron microscopy (TEM; JEM-2100, JEOL Ltd., Japan), X-ray polycrystalline diffractometer (XRD; Smartlab 9kW, Rigoku, Japan), UV-Vis spectrophotometer (UV-Vis; UV-1750, SHIMADUZ, Japan), Fourier transform

infrared spectrometer (FTIR; NEXUS-870, Nicolet Instrument Co., USA), X-ray photoelectron spectroscopy (XPS; ES-CALAB 250, Thermo Ltd., USA) were used. All electrochemical measurements were conducted on a CHI660D electrochemical workstation (Shanghai CH Instrument Co., Ltd., China). All ECL data were collected with MPI-A analyzer (Xi'An Remax Electronic Science & Technology Co., Ltd., China). Electrochemical impedance spectroscopy (EIS) analysis was performed on the Thales electrochemical workstation. In this work, Ag/AgCl electrode was used as reference electrode, platinum wire electrode as auxiliary electrode and glassy carbon electrode (GCE) as working electrode.

## Results and discussion

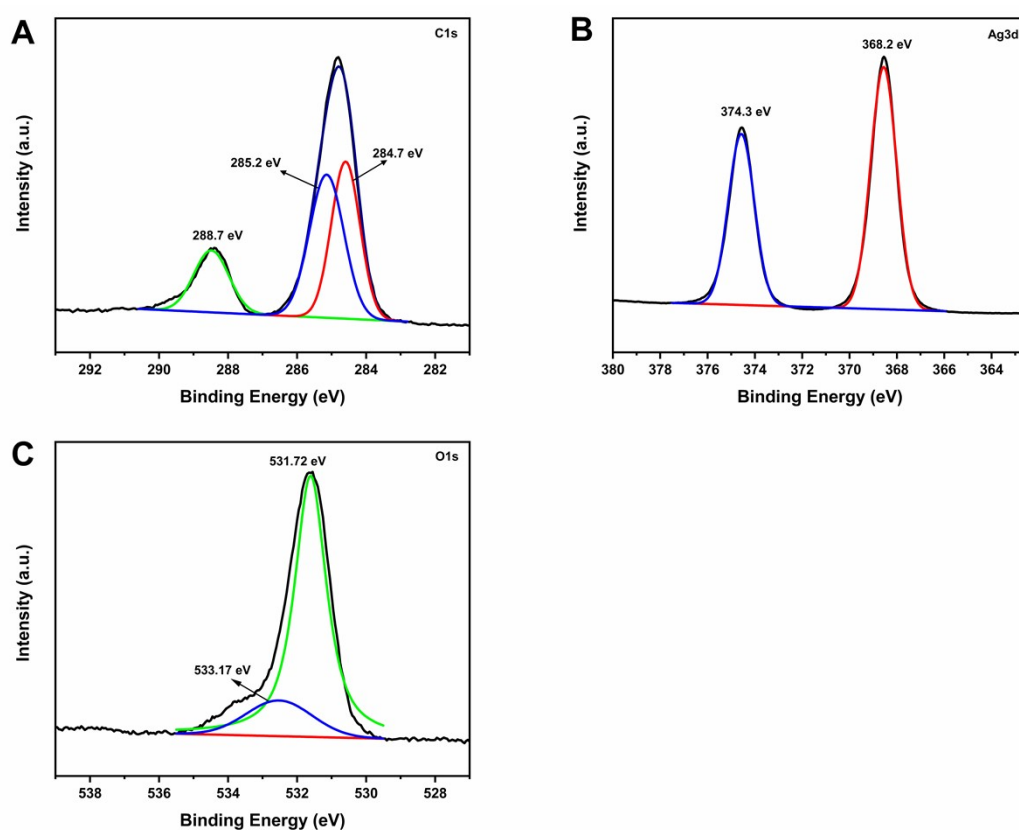


Figure S1 (A) C1s spectrum of Ag-MOF; (B) Ag3d spectrum of Ag-MOF; (C) O1s spectrum of Ag-MOF.

In order to obtain the best test performance, a series of experimental conditions of the sensor were optimized. Including proportion of materials, concentration of  $K_2S_2O_8$ , the concentration and incubation time of the mercury ion aptamer, mercury ions incubation time, the concentration and incubation time of streptavidin.

The amount of Au NPs was optimized in the range of 2  $\mu$ L to 10  $\mu$ L. As shown in Figure S2A, the ECL intensity reached a maximum when 4  $\mu$ L of Au NPs were modified. The concentration of  $K_2S_2O_8$  was optimized in the range of 0.06 to 0.14 M (Figure S2B). When the concentration exceeded 0.1 M, the ECL intensity tended to be stable with the concentration. Therefore, we chose to drop 4  $\mu$ L of Au NPs on the electrode and followed by detection in 0.1 M  $K_2S_2O_8$ . Then as shown in Figure S2C, when the concentration was in the range of 0.5  $\mu$ L to 2.5  $\mu$ L, the ECL intensity decreased after modification of the mercury ion aptamer due to steric effect. And the ECL intensity tended to be stable after increasing the concentration to 1.5  $\mu$ L. Therefore, the mercury ion aptamer concentration of 2  $\mu$ M was selected as the best experimental conditions. With the increase of aptamer incubation time in the range of 30 min to 80 min, the ECL intensity also decreased gradually and reached stable after 60 min (Figure S2D). 70 min was selected as the experimental condition. It could get from Figure S2E that with the increase of incubation time of mercury ions in the range of 60 min to 100 min, ECL response gradually increased due to the detachment of the aptamer from the electrode surface. The ECL intensity tended to be stable after 80 min. We chose 90 min as the best incubation time. The ECL intensity was further reduced after streptavidin modification due to increased steric hindrance. With the

increase of its concentration from  $0.3 \text{ mg}\cdot\text{mL}^{-1}$  to  $2.0 \text{ mg}\cdot\text{mL}^{-1}$ , the intensity tended to be stable after modification with  $1.0 \text{ mg}\cdot\text{mL}^{-1}$  of SA (Figure S2F). When the incubation time of streptavidin on the electrode increased in the range of 5 min to 25 min, the ECL intensity also decreased. After 20 minutes, the ECL intensity tended to be stable (Figure S2G). We finally chose the concentration of  $1.5 \text{ mg}\cdot\text{mL}^{-1}$  and incubation for 20 min as the best experimental condition.

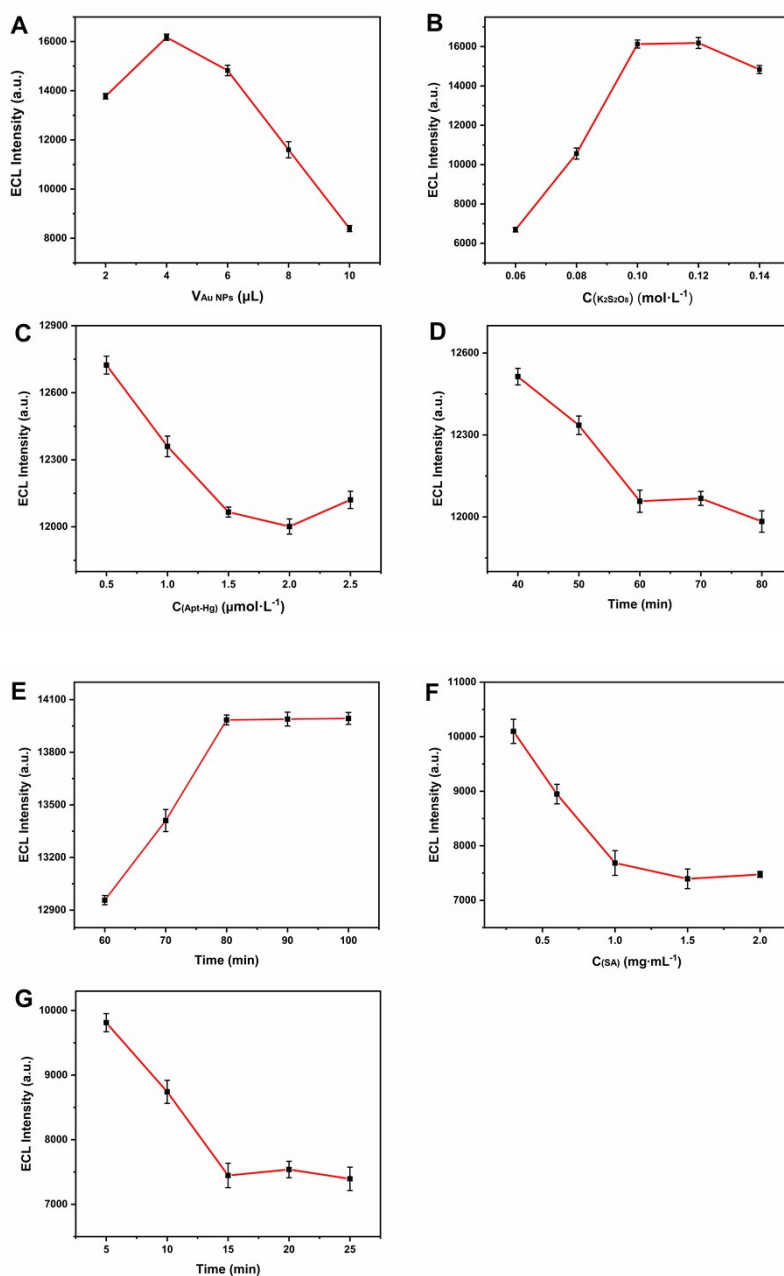


Figure S2. Effect of (A) volume of Au NPs; (B) concentration of  $K_2S_2O_8$ ; (C) concentration of Apt-Hg; (D) incubation time of Apt-Hg; (E) Effect of incubation time of  $Hg^{2+}$ ; (F) concentration of SA; (G) incubation time of SA.

According to the results of XRD pattern and morphology of Ag-MOF, the crystal structure of Ag-MOF could be obtained as the following figure<sup>[1]</sup>.

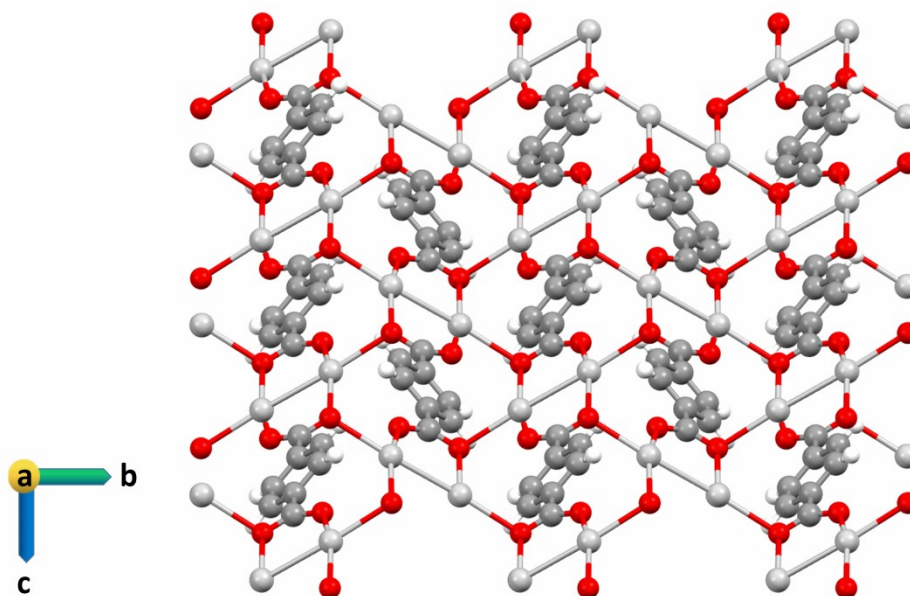


Figure S3 Crystal structures of Ag-MOF from the CIF file [CCDC: 198096].

## References

- [1] Shalini, S. S.; Balamurugan, R.; Velmathi, S.; Bose, A. C., Systematic Investigation on the Electrochemical Performance of Pristine Silver Metal-Organic Framework as the Efficient Electrode Material for Supercapacitor Application. *Energy Fuels* 2022, 36 (13), 7104-7114.