Electronic Supplementary Material (ESI) for Analytical Methods.
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Supplementary Material

A Label-free electrochemical aptasensor based on NH_2-MIL-235(Fe) for the sensitive detection of Citrinin

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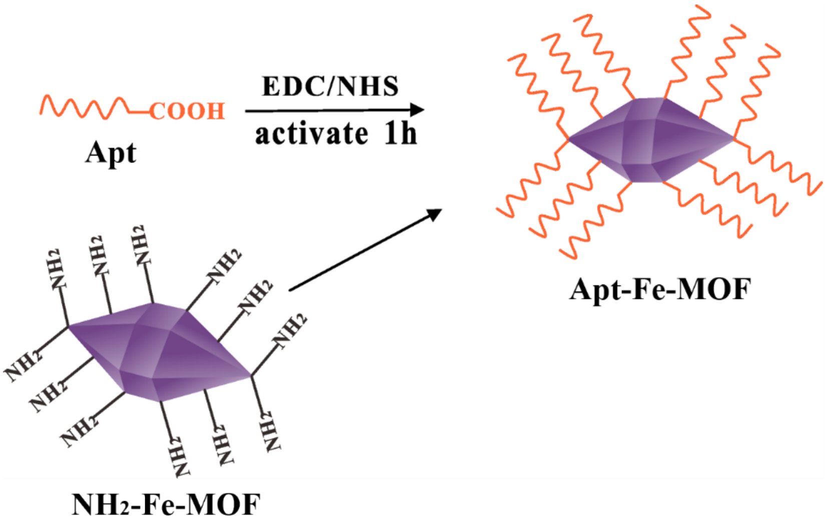
S1 Reagent, materials and apparatus

N-hydroxyl thiosuccinimide sodium salt (NHS), 1-Ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride (EDC), and FeCl3·6H2O were purchased from Shanghai Yuanye Biotechnology Co., Ltd. (Shanghai, China). 2-amino terephthalic acid (NH_2-BDC) was purchased from Alfa Aesar Co., Ltd. (Shanghai, China). Citrinin (CIT), aflatoxin B1(AFB1), zearalenone (ZEN), fumonisin B1(FB1), deoxynivalenol (DON), were purchased from Shanghai Yuanye Bio-Technology Co, Ltd. (Shanghai, China).

The CIT aptamer sequence: 5’ - COOH -GGC CAG GCG GGG CCT GTT CGT GGG CCG TGT CTT CGG CTC GCT CGG TTG - 3’were synthesized by Sangon Biotech Co, Ltd. (Shanghai, China)

Electrochemical impedance spectroscopy (EIS) and differential pulse voltammetry (DPV) were carried out in a CHI 660E workstation (Shanghai Chen Hua Instrument Co., Ltd., Shanghai, China) with a traditional three-electrode system, where a platinum wire electrode was used as a counter electrode, a saturated calomel electrode was used as a reference, and the modified AuE was used as the working electrode. Electrochemical impedance spectroscopy (EIS) was performed in 5 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl, and differential pulse voltammetry (DPV) was measured in 5mM $[Fe(CN)_6]^{3-/4-}$ in PBS (20mM,PH=7.4) solution. In the case of EIS, the frequency range is from 0.1 to 100000 Hz and the amplitude is 0.005 V. In the case of DPV, the scan rate, amplitude, interval and modulation times are 0.02 v/s, 0.05 v, 0.2 s and 2 s, respectively. Transmission electron microscopy (TEM) images were obtained with an HT7700 transmission electron microscope from Japan Hitachi Co., Ltd. (Tokyo, Japan). The scanning electron microscopy (SEM) was recorded with Quanta Feg 250 scanning electron microscopy from Japan Hitachi Co., Ltd. (Tokyo, Japan).

S2 Preparation of Apt-Fe-MOF



Scheme 1. Preparation of Apt-Fe-MOF;

S3 Electrode Benchmarking

The electrode had been benchmarked by using the Randle-Sevcik equation[1, 2]:

$$Ip = 2.69 \times 10^5 \times n^{3/2} \times A \times D^{1/2} \times C \times v^{1/2}$$

where n is the number of electrons transferred, D is $[Fe(CN)_6]^{3-/4-}$ diffusion coefficient, C is the concentration of $[Fe(CN)_6]^{3-/4-}$ solution and A is the electrode surface area. It was calculated that A for the area of the electrode modified with Apt-Fe-MOF/AuE was 0.0899 cm^2. The bare AuE was 0.131 cm^2, which was about 1.46 times that of the Apt-Fe-MOF/AuE electrode. These results indicate that the insulated Apt-Fe-MOF composite hinders the electron transfer at the solid/liquid interface reducing the real electroactive area.

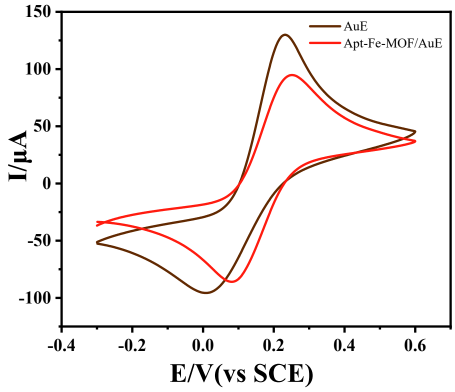


Fig.1 CV of AuE and Apt-Fe-MOF

S4 Calculation method of detection limit

In this experiment, we calculated LOD according to the recommendations of the International Union of Pure and Applied Chemistry (IUPAC): the analyte's signal at the detection limit (Sdl) is calculated according to the formula:

$$Sdl = Sreag + 3 * \sigma reag$$

where Sreag is the electrochemical signal for a blank, σreag is the known standard deviation for the blank's electrochemical signal (n_σ=8). Finally, the aptasensor's limit of detection is calculated by the above data and calibration curves.

S5 The pretreatment of the corn sample

Firstly, disperse 5 g of corn flour in 20 mL of acetonitrile-water (70%, v/v) solution and sonicate for 2 min. After standing for 10 min, centrifuge at 10,000 rpm for 15 min twice. Finally, it was diluted 100 times with PBS, and the supernatant was taken as a corn sample. Finally, the prepared corn samples were used as CIT standard solutions diluted with different concentrations.

Reference :

1. B. Rezaei and S. Damiri, *Sensors and Actuators B: Chemical*, 2008, **134**, 324-331.
2. A. Garcia-Miranda Ferrari, C. W. Foster, P. J. Kelly, D. A. C. Brownson and C. E. Banks, *Biosensors (Basel)*, 2018, **8**.