Supporting Information

1. Experimental section

1.1. Materials and reagents

All oligonucleotides, including the OTA aptamer (OPT), DNA capture probe (CP), DNA helper strands (HS), signal probe 1 (S1), and signal probe 2 (S2), were customized and purified by Sangon Biotech Co., Ltd. (Shanghai, China). The sequence information is described in Table S1.

Table S1. Oligonucleotides used in this study.

Name	Sequence（5'-3'）
OPT	GAT CGG GTG TGG GTG GCG TAA AGG GAG CAT CGG ACA
CP	HS-C6-TAT CAC CAG GCA GTT CGC CAC CCA CAC CCG ATC
HS	TGT CCG ATG CTC CCT TTA AAC TGC CTG GTG ATA
S1-MB	HS-C6-GAT CGG GTG TGG-MB
S2-MB	MB-GAG CAT CGG ACA- C6-HS

Ammonium tetrathiomolybdate [$(NH_4)_2MoS_4$], 6-mercaptohexanol (MCH), and poly-(diallyldimethylammonium chloride) (PDDA, 20 wt %) were purchased from Sigma Chemical Co., Ltd. (St. Louis, MO, USA). Graphene oxide (GO) was purchased from Suzhou Hengqiu Co., Ltd. (Suzhou, China) The monodispersed silica spheres (SiO_2, D=500 nm) were obtained from Alfa Asear. Ferrocene, acetone, ethanol, hydrogen peroxide (H_2O_2), sodium citrate, and hydrofluoric acid (HF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Potassium ferricyanide ($K_3[Fe(CN)_6]$), potassium chloride (KCl), and potassium ferrocyanide ($K_4[Fe(CN)_6]$) were all obtained from Shanghai Linfeng Chemical Reagent Co., Ltd. (Shanghai, China). Chloroauric acid hydrate ($HAuCl_4 \cdot 4H_2O$) was purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Ochratoxin A (OTA), Aflatoxin B1 (AFB1), Aflatoxin B2 (AFB2), AflatoxinM1 (AFM1), and Zearalenone (ZEN) were purchased from Pribolab Pte. Ltd. (Singapore). All other chemicals were of analytical grade and used without further purification. A stock solution of 3% PDDA was prepared in the mixture of Tris and NaCl. A total of 0.01 M pH 7.4 phosphate buffered solution (PBS) was used as the electrolyte in this work. Double-distilled water (DDW) was used throughout the experiments.

The surface morphology of the 3DOM MoS_2-AuNPs electrode was investigated by scanning electron microscopy (SEM, Hitachi S4800). The elemental composition analysis was performed by energy dispersive X-ray spectroscopy (EDS Falcon 60S, EDAX Inc.). Transmission electron microscopy (TEM) images were obtained from a JEOL JEM-200CX microscope. CV, EIS, and DPV were carried out on a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Company, China). The typical three-electrode cell system consisting of a saturated calomel reference electrode (SCE), a 3DOM RGO-AuNPs-MoS_2 modified Au slice working electrode, and a Pt auxiliary electrode was used for all the electrochemical measurements. All electrochemical experiments were purged with high-purity N_2 to remove O_2.

1.2. Fabrication of the composite of AuNPs-Fe_3O_4@C

The Fe_3O_4@C composite was prepared with slight modifications based on a previously reported method [1]. Briefly, 0.12 g of ferrocene was dissolved in 40 mL of acetone and sonicated for 40 min. Then, 2 mL of 30% hydrogen peroxide was added, and the mixture was stirred for 30 min. The resulting mixture was transferred to a 100 mL poly tetrafluoroethylene reaction kettle and reacted at 250 °C for 36 h. After cooling to room temperature, the black product was obtained by magnetic separation, washed alternately with water and ethanol, and then dried under vacuum at 60 °C for 8 h. Finally, the product was calcined at 750 °C for 2 h under an argon atmosphere, followed by thermal oxidation at 250 °C for 6 h under an air atmosphere.

AuNPs were prepared with slight modifications according to the literature [2]. A total of 200 mL (0.01%, w/w) $HAuCl_4 \cdot 4H_2O$ was poured into a three-necked round-bottom flask and heated to boiling with rapid stirring. Then, 5 mL (1%, w/w) sodium citrate was quickly added to the boiling solution and continuously stirred for 10 min. Subsequently, the heating was stopped, and the stirring was continued for 15 min. Finally, the obtained AuNPs were transferred to a conical flask and stored in the dark for future use.

To prepare the AuNPs-Fe_3O_4@C composite, 0.02 g of Fe_3O_4@C was mixed in a solution of 40 mL of ethanol and water (volume ratio of 1:1) by ultrasonication for 30 min. Then, 15 mL of 3% PDDA solution was added to the above solution under stirring for 30 min, and the residual PDDA was removed by magnetic separation. Finally, the composite was dissolved in 50 mL of AuNPs solution and stirred for 10 h. The unadsorbed AuNPs were removed by magnetic separation, and the resulting purple-black AuNPs-Fe3O4@C was dispersed in 0.01 M pH 7.4 PBS to obtain a dispersion with a concentration of 25 mg/mL for further use.

1.3. Fabrication of the Biocomposite of S1/S2-AuNPs-Fe_3O_4@C

In order to prepare S1/AuNPs-Fe_3O_4@C and S2/AuNPs-Fe_3O_4@C, 20 mL of the previously prepared AuNPs-Fe_3O_4@C dispersion was taken and mixed with 50 μL of 50 μM S1-MB, followed by overnight oscillation at 37 °C. The resulting mixture was subjected to magnetic separation to obtain S1/AuNPs-Fe_3O_4@C, which was then dispersed in 1 mL of PBS and stored at 4 °C for later use. Similarly, S2/AuNPs-Fe_3O_4@C was prepared using the same method. To facilitate signal amplification comparison, S1/AuNPs and S2/AuNPs were also prepared.

1.4. Electrochemical measurement

The CV curves were measured between -0.2 and 0.6 V, with a scan rate of 0.1 V/s. The EIS measurements were made with an AC amplitude of 0.005 V and a frequency range of 100k Hz to 0.05 Hz. The CV and EIS of the working solution was 5 mM $[Fe(CN)_6]^{3-/4-}$ containing 0.1 M KCl. The DPV was measured between -0.5 and 0 V at a scan rate of 0.1 V/s. The DPV of the working solution was 0.01 M pH 7.4 PBS.

1.5. Real samples preparation

The rice and wheat powder samples were provided by the National Light Industry Food Quality Supervision and Inspection Station of Nanjing. Firstly, the rice was pulverized using a grinder to obtain the powder sample. Then, 5 g of the rice or wheat powder sample was added to a 50 mL centrifuge tube, followed by the addition of 15 mL of extraction solution (80% methanol and 4% NaCl). The resulting mixture was shaken for 45 min and then centrifuged at 4000 rpm for 5 min at room temperature [3,4]. The supernatant was collected and diluted tenfold with distilled water. Finally, different standard concentrations of OTA were added to the diluted solution to obtain the test samples.

References

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