Supplementary Material

A magnetic plasma Fe_3O_4@Cu@Cu_2O photoelectrochemical sensor for the detection of fumonisin B1

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Materials and Reagents

Alpha fetoprotein (AFP), prostate specific antigen (PSA), Cytokeratin 19 fragment 21–1 (CYFRA21-1), brain natriuretic peptide (BNP), procalcitonin (PCT) and FB1 were gained from Shanghai Linc-Bio Science Co. LTD, (Shanghai, China). FB1 aptamer, NH_2-DNA_1, SH-DNA_2 were gained from Sangon Biological Engineering Technology & Company Ltd. (Shanghai, China).

Synthesis of Fe_3O_4@Cu@Cu_2O

Fe_3O_4@Cu@Cu_2O nanocomposites were successfully prepared by a simple one-step solvothermal method with appropriate modifications. Typically, 1 mmol copper sulfate pentahydrate (0.25 g), 2 mmol ferric chloride hexahydrate (0.54 g), and 20 mmol sodium acetate trihydrate (2.7 g) were dissolved in 25 mL glycol solution under magnetic agitation. The acquired solution was then transferred to a 50 mL teflon lined stainless steel high-pressure reactor and heated at 200 ℃ for 10 h. After natural cooling to room temperature, the products were collected by an external magnetic field, washed three times with water and ethanol, and dried in a 60 ℃ vacuum drying oven.

Synthesis of CdS

CdS nanomaterials were successfully prepared using a simple one-step solvothermal method. At room temperature, 20 mmol cadmium chloride (4.56 g) and 4 mmol thioacetamide (0.30 g) were dissolved in 60 mL isopropyl alcohol solution by magnetic agitation, and then the resulting solution was transferred to 100 mL polytetrafluoroethylene lined stainless steel high-pressure reactor and heated at 180

℃ for 18 h. After being naturally reduced to room temperature, the product was washed three times with anhydrous ethanol and ultra-pure water. Finally, the product was placed in a vacuum drying oven at 60 °C and dried overnight to obtain CdS nanoparticles.

Preparation of Fe_3O_4@Cu@Cu_2O-DNA_1 hybrids

Firstly, 1 mL Fe_3O_4@Cu@Cu_2O suspension was mixed with chitosan acetic acid (3 mL, 0.1wt %) solution, and then reacted at 50 ℃ for 2 h. Then, after washing with ultra-pure water, it was dispersed into glutaraldehyde aqueous solution (3 mL, 5wt %), and heated at 38 ℃ for 1 h. The product was obtained by magnetic separation. Add 1mL of 100 nmol L^{-1} NH_2-DNA_1, incubate at 2 ℃ for 12 h, and finally add monoethanolamine, get Fe_3O_4@Cu@Cu_2O-DNA_1 at 2 ℃.[1]

Preparation of DNA_2-CdS hybrids

125 mg of CdS was placed in 25 mL of ethanol/water solution at a volume ratio of 19:1. Then, 1 mL of trimethylol aminomethane hydrochloride buffer solution was added to the CdS suspension and sonicated at 70 ℃ for 20 min to obtain a mixed suspension. After cooling, the suspension was centrifuged and washed three times with ethanol. The amino-functionalized CdS was obtained by redispersing it in 5 mL of ultrapure water. Stir at room temperature for 12h, then 10 μL of SH-DNA was added to the solution, after this stirred for 10 h, centrifuged and washed three times with ultrapure water to obtain DNA_2-CdS.[2]

Preparation of Fe_3O_4@Cu@Cu_2O-DNA_1-FB1 aptamer-DNA_2-CdS hybrid immune complex

At 37 ℃, within 1 h, a partial hybridization reaction was performed to form 1 mL 200 nmol L^{-1} DNA_2-CdS and 1 mL 200 nmol L^{-1} FB1 antigen aptamer solution containing 20 mmoL L^{-1} $MgCl_2$ and 1 mL 200 nmol L^{-1} $MgCl_2$. The partial hybridization reaction of Fe_3O_4@Cu@Cu_2O-DNA_1-FB1 aptamer-DNA_2-CdS hybrid immunocomplex was extracted and washed with external magnetic field and dispersed in 1 mL ultra-pure water. The immunohybridization of Fe_3O_4@Cu@Cu_2O-DNA_1-FB1 aptamer-DNA_2-CdS hybrid was obtained.

Photoelectric chemical detection

The photocurrent is measured on the PEC workstation (Shanghai CHI 760E Chenhua Instrument Company, China). Silver/silver chloride electrode (Ag/AgCl) was used as reference electrode, and platinum electrode was used as counterelectrode for detection in trimethylol aminomethane hydrochloride buffer solution (pH = 7.4). The excitation light is an LED lamp (450 nm) with a voltage of 0 V(vs. Ag/AgCl), which is switched every 10 s.

Table S1. Samples analysis of FB1.

Samples	Addition (ng/mL)	Found (PEC) (ng/mL, n=5)	RSD (n=5, %)	Recovery (n=5, %)
Vinegar	10.00	10.12	2.8	101.2
	30.00	29.54	3.7	98.5
	50.00	49.56	4.1	99.1

References

[1] S.J. Zhao, Z. Song, T. Liu, X. Wang, Y.X. Li, Y.Q. Xu, H. Wang, Y. Wu and X.L. Luo, *Sensors and Actuators B: Chemical*, 2023, **378**. 133166.
[2] Z. S. Dawood, Z. Moazzam and T. M. Pawlik, *Annals of Surgical Oncology*, 2023, **30**, 275-276.