Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic Supplementary Material

A ratiometric electrochemical strategy based on Fe (III) and Pt (IV) for immobilization-free detection of Escherichia coli

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Synthesis of Magnetic $CuFe_2O_4$ Nanoparticles

Magnetic $CuFe_2O_4$ nanoparticles were prepared by a facile solvothermal method [1].Briefly, NaAc (0.36 g), $FeCl_3 \cdot 6H_2O$ (0.135 g, 0.5 mmol), and $CuCl_2 \cdot 2H_2O$ (0.0425 g, 0.25 mmol) were completely dissolved in ethylene glycol (EG, 5.0 mL) via ultrasonication for 40 min. Then, the obtained homogeneous mixture solution was transferred into a Teflon-lined stainless-steel autoclave and sealed to heat at 200°C for 8h. After the reaction, the magnetic CuFe2O4nanoparticles were obtained with the help of a magnet, rinsed with ultrapure water and ethanol several times, and finally dried for later use.

Synthesis of $CuFe_2O_4$/GO composite

The $CuFe_2O_4$/GO nanocomposite was prepared by a versatile self-assembly approach [2]. Briefly, 1 mg/mL of GO was dispersed in deionized water and sonicated for 2 h to form a brown GO aqueous solution for later use. And as-prepared $CuFe_2O_4$ nanoparticles was dispersed in deionized water with sonication for 1 h to be a homogeneously dispersed suspension with a concentration of about 2 mg /mL, and the pH value of this suspension was adjusted to four using 0.1 mol L^{-1} HCl solution. Subsequently, the resulting GO aqueous solution was then added to the above suspension dropwise and the mixed solution was sonicated for another 2 h. Finally, the obtained $CuFe_2O_4$/GO nanocomposite was centrifuged, washed, and dried.

Synthesis of PANI/$CuFe_2O_4$/GO composite

As far as we know, there are no reports on the synthesis of PANI/$CuFe_2O_4$/GO nanocomposites. So we prepared the PANI/$CuFe_2O_4$/GO composite by the synthesis method of PANI/$CuFe_2O_4$ by Hassan et al [3] and modified slightly. The polyaniline copper ferrite nano-composite was prepared using chemical polymerization method by dispersing 0.2 g of the previously prepared $CuFe_2O_4$/GO composite in 20 mL of 2M HCl and stirred vigorously at room temperature for 10 min. 1.25 mL aliquot of distilled aniline monomer was added under continuous stirring for 30 min. To the above suspension, 5 mL of 19.7 mmol $(NH_4)_2S_2O_8$ was added drop-wisely, as a polymerization initiator. An immediate color change of the solution to blue green was observed. The suspension was stirred to complete the polymerization process for about 1 h. The composite was separated by magnet, rinsed with distilled water, and finally dried at 100 ℃.

Synthesis of Au NPs

The Au NPs were synthesized according to Ma's method [4] in short one milliliter of chloroauric acid solution (1 wt %) was added into deionized water to dilute to 100 mL and heated with stirring. After boiling, a sodium citrate solution (1 wt %, 2.5 mL) was added dropwise into the diluted solution. The solution was continuously heated for 5 min until it turned wine red. The solution was then transferred to a 4°C environment for storage.

Bacteria culture and preparation

E. coli strain (DH 5α, provided by Zhenglin Gao, 402 Biological Laboratory, College of Pharmacy, Guizhou University) were cultured in broth culture medium (Luria-Bertani (LB) medium including Tryptone, Yeast, NaCl, Ph=7) until an optical density between 1.0 and 1.3 was obtained. Growth medium was got rid of by centrifugation (3000 rpm, 15 min) and resuspension in PBS (KH_2PO_4, Na_2HPO_4, NaCl; 0.1 M, pH 7.4). The number of bacteria in solution was determined by optical density (OD) at a wavelength of 600 nm, OD600 value of 1.0 is corresponding to the bacteria concentration of 8×10^8 colony forming units (cfu/mL), and the E. coli solution was diluted 10 times, 100 times and so on [5]. S. aureus, B. subtilis, E. coli strains were cultured with the same method as above (provided by Lei Wang, 404 Biological Laboratory, College of Pharmacy, Guizhou University)

Characteristics of the Prepared Nanomaterials

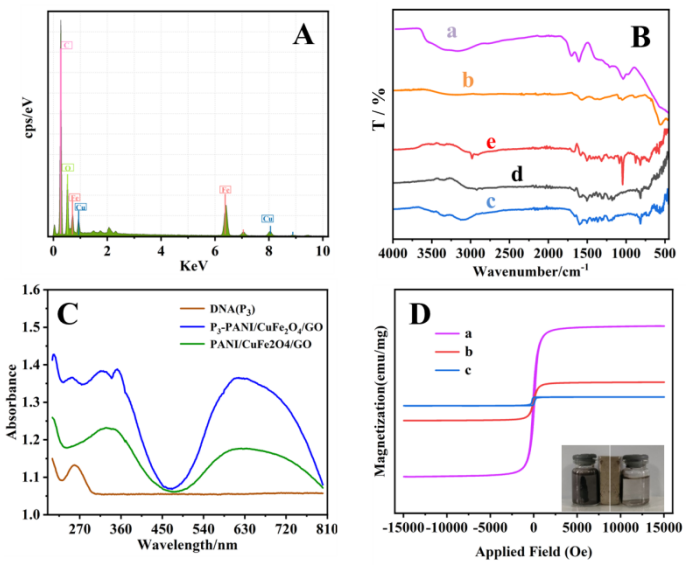

Fig. S1 EDS spectrum of $CuFe_2O_4$ (A), FT-IR spectroscopy of composites (B): (a) GO, (b) $CuFe_2O_4$, (c) $CuFe_2O_4$/GO, (d) PANI/$CuFe_2O_4$/GO, (e) NH_2-PANI/$CuFe_2O_4$/GO. UV–vis absorption spectra of composites (C), Magnetization hysteresis loops of composites (D): (a) $CuFe_2O_4$, (b) $CuFe_2O_4$/GO, (c) PANI/$CuFe_2O_4$/GO.

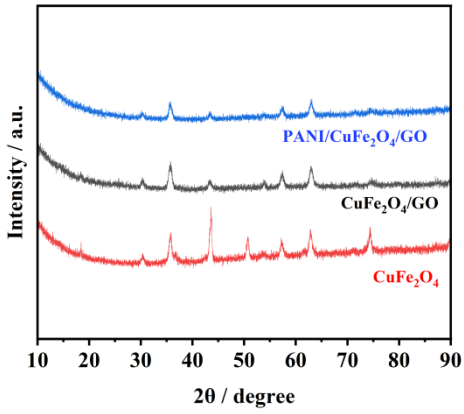

Fig. S2 XRD pattern of $CuFe_2O_4$, $CuFe_2O_4$/GO, PANI/$CuFe_2O_4$/GO.

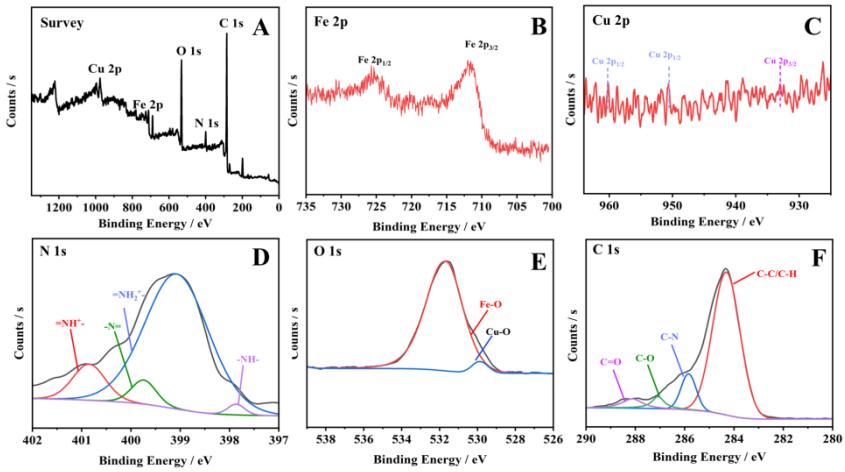

Fig. S3 XPS spectra of PANI/$CuFe_2O_4$/GO composite: survey spectrum (A), Fe 2p spectrum (B), Cu 2p spectrum (C), N 1s spectrum (D), O 1s spectrum (E) and C 1s spectrum (F).

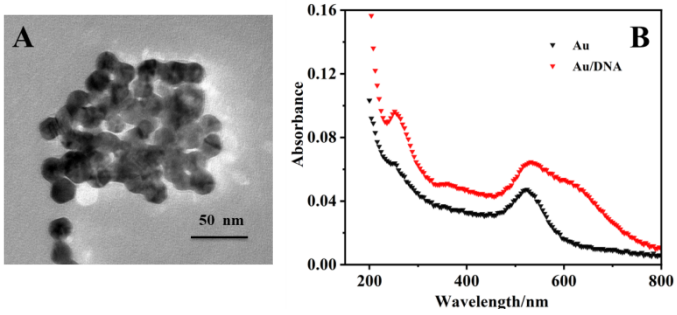

Fig. S4 TEM images of Au NPs (A), UV–vis absorption spectra of Au NPs and tDNA/Au.

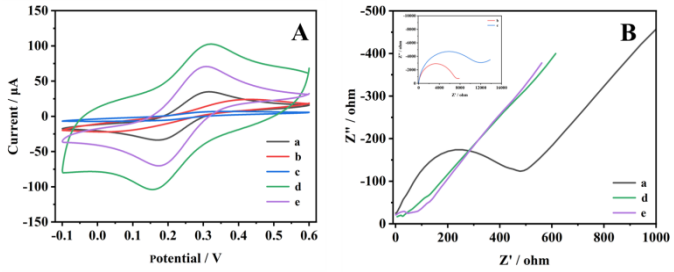

Fig. S5 (A) The CV curves of different modified electrodes in 5 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl (scanning rate: 50 mV/s): (a) bare GCE; (b) $CuFe_2O_4$/GCE; (c) GCE+$CuFe_2O_4$/GO; (d) GCE+$CuFe_2O_4$/GO-PANI; (e) cDNA-PANI/$CuFe_2O_4$/GO. (B) EIS curves (Nyquist) of work electrode modified with different materials in 5 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl: a) bare GCE; (b) $CuFe_2O_4$/GCE; (c) GCE+$CuFe_2O_4$/GO; (d) GCE+$CuFe_2O_4$/GO-PANI; (e) cDNA-PANI/$CuFe_2O_4$/GO.

Feasibility of the Designed Strategy

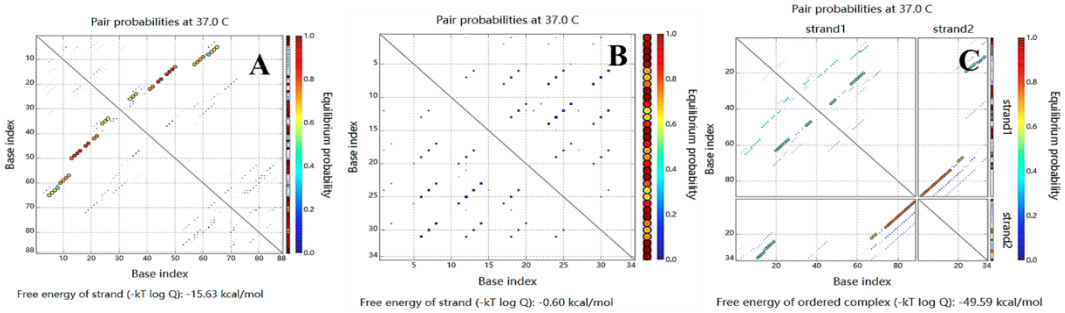

Fig. S6 NUPACK analysis of binding of DNA strands: (A) aDNA, (B) tDNA and (C) binding of aDNA and tDNA.

Optimization of the Experimental Conditions

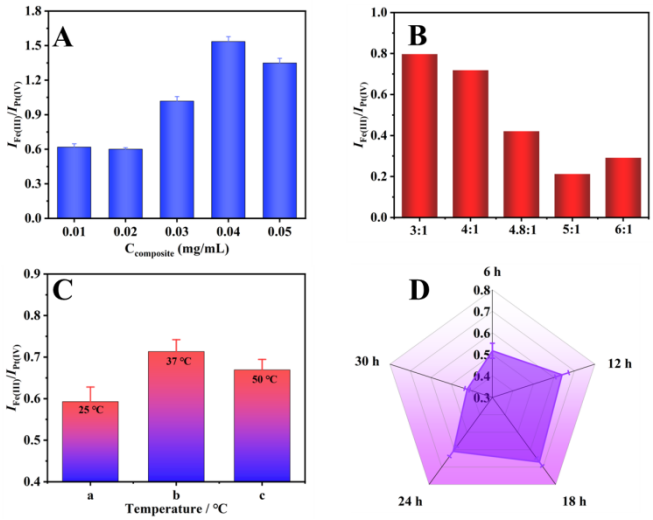

Fig. S7 Optimization of the experimental conditions: the amount of cDNA-PANI/$CuFe_2O_4$/GO composite (A), the different ratios of Pt (IV) and Fe (III) (B), the reaction temperature (C) and the adsorption time of DNA/Au NPs for Pt (IV) (D).

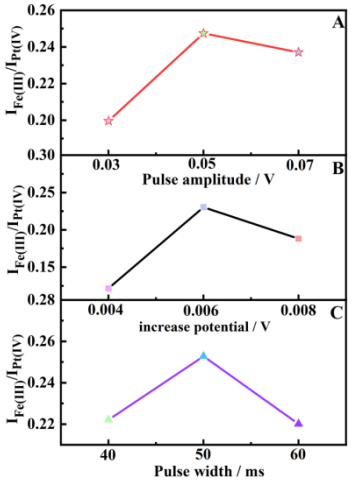

Fig. S8 DPV measurements optimization: pulse amplitude (A), increase potential (B), pulse width (C).

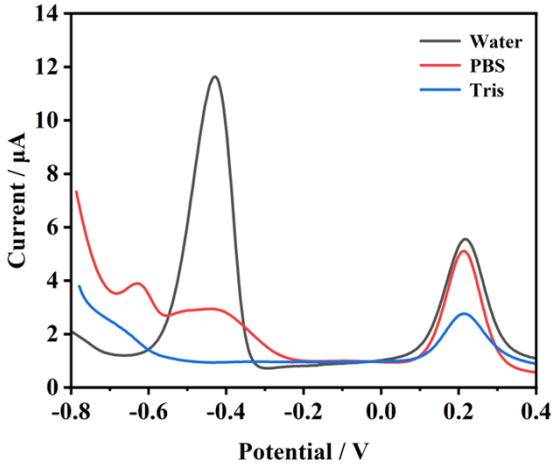

Fig. S9 DPV signal response of different solution.

Real Samples Analysis

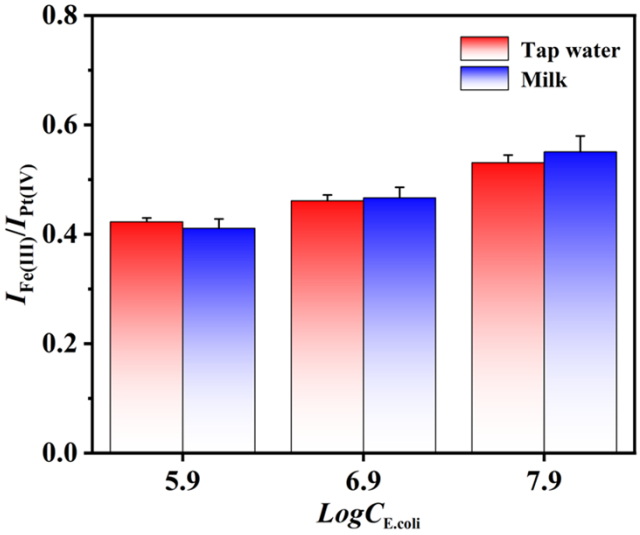

Fig. S10 The DPV response obtained for milk samples spiked with DH 5α.

Table S1 Oligonucleotide sequences used in this work

Oligo Name	Sequence (from 5' to 3')
cDNA	COOH-ATCCGTCACACCTGCTCTATCAAATGTGCAGATATCAAGACGATTTGTACAAGATGGTGTTGGCTCCCGTAT
aDNA	ATCCGTCACACCTGCTCTACGGCGCTCCCAACAGGCCTCTCCTTACGGCATATTATGGTGTTGGCTCCCGTATCCCTAACCCTAACCC
tDNA	SH-AGGGTTAGGGTTAGGGTTAGGGTTAGGGTTAGGG

Table S2 Analytical performances of various methods towards E. coli

Assay	Linear range	Detection limit	Materials	Reference
Electrochemistry	1- 4×10^4 cfu/mL	1 cfu/mL	Nitrocellulose-modified Gr electrodes	[6]
Electrochemistry	10^6-10^8 cfu/mL	10^5 cfu/mL	Au/FTO	[7]
Electrochemistry	10-10^8 cells/mL	1 cell/mL	RS-PVA gel, Label-free	[8]
Electrochemistry	1-1×10^3 cfu/mL	27 cfu/mL	Amine modified thermoplastic electrodes	[9]
Electrochemistry	10^3-10^6 cfu/mL	10^3 cfu/mL	Antibody immobilized on gold electrodes	[10]
Electrochemistry	8×10^3-8×10^8 cfu/mL	1.862×10^3 cfu/mL	DNA/PANI/$CuFe_2O_4$/GO, immobilization-free	This work

References

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