Supplementary Information (SI) for Analytical Methods.
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Supporting Information

Aptamer sensor based on peroxidase-like AgNPs@MOF for SERS and colorimetric dual-mode detection of sulfadimethoxine

Renjie Zhao [a1], Zhanye Yang [a1], Xin Sun [b], Guantong Liu [c], Shutong Zhang [a], Yuru Wang [a], Xinge Ju [a], Yuan Tian [a, *], Lan Ding [a, *], Daqian Song [a]

[a] College of Chemistry, Jilin Province Research Center for Engineering and Technology of Spectral Analytical Instruments, Jilin University, Changchun, 130012, P. R. China

[b] Jilin Provincial Traffic Information and Communication Center, Changchun, 130021, P. R. China

[c] College of Chemistry, Jilin University, Qianjin Street 2699, Changchun 130012, P. R. China

* Corresponding author.

Phone: +86-431-85168473;

Fax: +86-431-85193421

E-mail: tianyuan@jlu.edu.cn (Yuan Tian); dinglan@jlu.edu.cn (Lan Ding)

Reagents and instruments

Silver nitrate ($AgNO_3$) and iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were purchased from Beijing Dingguo Biotechnology Co., LTD. Potassium carbonate (K_2CO_3), nitric acid (HNO_3) and acetic acid (HAc) were purchased from Sinopharm Chemical Reagent Co., LTD. Sulfadimethylpyrimidine (SMZ), sulfachlorpyridine (SCP), sulfathiazole (STH), sulfapyridine (SPD) were purchased from Tianjin Alta Technology Co., LTD., China. Sulfadimethoxine (SDM) was purchased from Shanghai Macklin Biochemical Co., Ltd. Penicillin G Potassium salt (Pen G), chloramphenicol (CAP), tannic acid (TA), 3,3',5,5' -tetramethylbenzidine (TMB) and free radical catcher 5,5' -dimethyl-1-pyrrolin-n-oxide (DMPO) were purchased from Shanghai Aladdin BioChem Technology Co., Ltd. Hydrogen peroxide (H_2O_2, 30%) was purchased from Beijing Beihua Fine Chemical Co., LTD. An SDM aptamer with sequences of 5′-GAGGGCAACGAGTGTTTATAGA-3′ was purchased from Sangon Biotech Co., Ltd. (Shanghai, China). All aqueous solutions were prepared with high purity deionized water (18.2 MΩ), along with HEPES buffer solutions (10 mM HEPES, 50 mM NaCl, 2.5 mM $MgCl_2$, pH = 7.5) and NaAc-HAc buffer solutions (0.1 M pH = 4).

Portable Raman spectrometer (Mini Ram, B&W TEK Opto-Electronic. Co., LTD) with excitation wavelength of 785 nm, laser power of 100 mW and single integration time of 10 s. Scanning electron microscope (SEM) images were recorded by HITACHI-SU8000 scanning electron microscope (HITACHI Co., Ltd., Japan). Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS)

experiments were carried out on a JEOL JEM-2100F TEM operated at 200 kV. The powder X-ray diffraction (XRD) analyses were carried out on a D8 ADVANCE diffractometer (Bruker Co., Germany). X-ray photoelectron spectra (XPS) measurements were conducted with an ESCALAB QXI spectrometer (Thermo Fisher Scientific Inc., USA). Ultraviolet-visible (Uv-vis) absorption spectra experiments were carried out by Cary 60 spectrometer (Agilent Technologies Inc., USA). Fourier transform infrared spectra (FT-IR) was recorded using KBr pellets on a Nicolet Avatar360 FT-IR spectrophotometer (Thermo Fisher Scientific Inc., USA) in the range of 4000-400 cm^{-1}. The Zeta (ζ) potentials were measured via photon correlation spectroscopy on a Nano ZS90 laser particle analyzer (Malvern Instruments, UK). Circular dichroism (CD) measurements were performed on a MOS-450 circular dichroism spectrometer (Bio-Logic, French). The X-band ESR spectra were recorded on Bruker E500 spectrometer. All pH values were measured with a PHS-3C pH-Meter (INESA Scientific Inc., China).

Preparation of MIL-101(Fe)

MIL-101(Fe) was synthesized by solvothermal method[1]. Firstly, $FeCl_3 \cdot 6H_2O$ (1.35 g, 2.45 mM) and terephthalic acid (0.412 g, 1.24 mM) were added into 30 mL DMF and stirred for 1 h to obtain a clear solution. Then the mixture was transferred into a Teflon vessel and heated at 110 °C for 20 h. The resulting mixture was isolated by centrifugation and washed with DMF and ethanol three times respectively to obtain the orange products. Excess reactants and impurities were removed by washing with DMF and ethanol three times, then washed with 60 °C hot ethanol for 2 h,

repeated for 3 times, centrifuged, and finally dried in a vacuum oven at 60 °C for 12 h.

Preparation of TA protected AgNPs

As previously reported in the literature[1], AgNPs of about 40 nm were prepared by using TA as a reducing agent to reduce $AgNO_3$. Briefly, 10 mg TA was dissolved in 9.5 mL water, followed by the adjustment of the pH to 7.0 with a 0.5 mol/L K_2CO_3 solution. Then, 0.5 mL $AgNO_3$ (0.2 mol/L) solution was slowly dropped into the above solution under stirring at 500 rpm. After reaction for 60 min at room temperature, a clay bank solution of AgNPs would be obtained.

Preparation of AgNPs@MOF

AgNPs@MOF were prepared using an in situ synthesis strategy[1]. First, 15 mg of MIL-101 (Fe) was dissolved into 9.5 mL of H_2O by ultrasonic treatment. Under vigorous stirring, 0.5 mL of 40 mg/mL TA solution was rapidly injected into the MIL-101(Fe) dispersion. After stirring for 20 seconds, a dark blue TA@MIL-101(Fe) product was obtained. The TA@MIL-101(Fe) was centrifuged and then washed three times with deionized water to remove excess TA molecules. The hydroxyl groups in the tannins complexed with the unsaturated iron ions on the surface of MIL-101(Fe) to form TA@MIL-101(Fe). Then, the obtained TA@MIL-101(Fe) was dissolved in 9.5 mL of H_2O and the pH of the solution was adjusted to 7.5 with 0.5 mol/L K_2CO_3. finally, 0.5 mL of 0.2 mol/L $AgNO_3$ solution was added slowly at 600 rpm and the whole process was added within 30 min. During the reaction, TA was used as a reducing agent to reduce Ag^+ to Ag^0, thus reducing AgNPs on the surface of MOFs.

After stirring for another 1 h at room temperature and centrifugation, the black product, AgNPs@MOF, was washed three times with distilled water to collect the black product AgNPs@MOF. Finally, the AgNPs@MOF was dried under vacuum at 80°C for 6 h, and then dispersed in ultrapure water to prepare a 1 mg/mL solution.

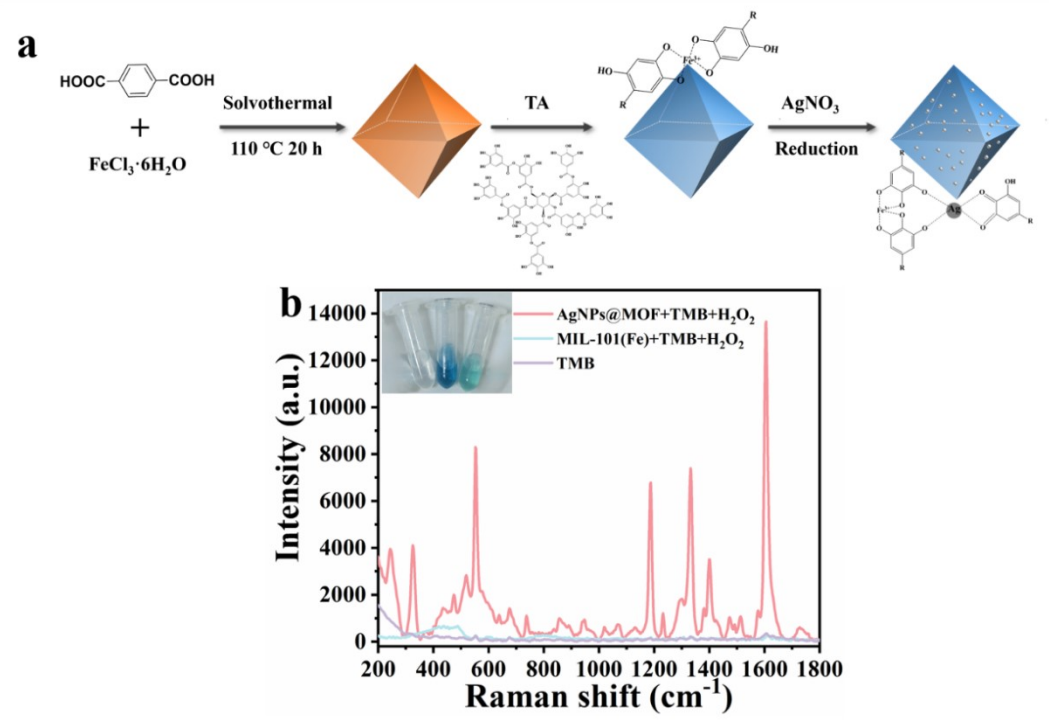

Fig. S1 (a) Synthesis process of AgNPs@MOF; (b) SERS spectra of TMB solution in different systems

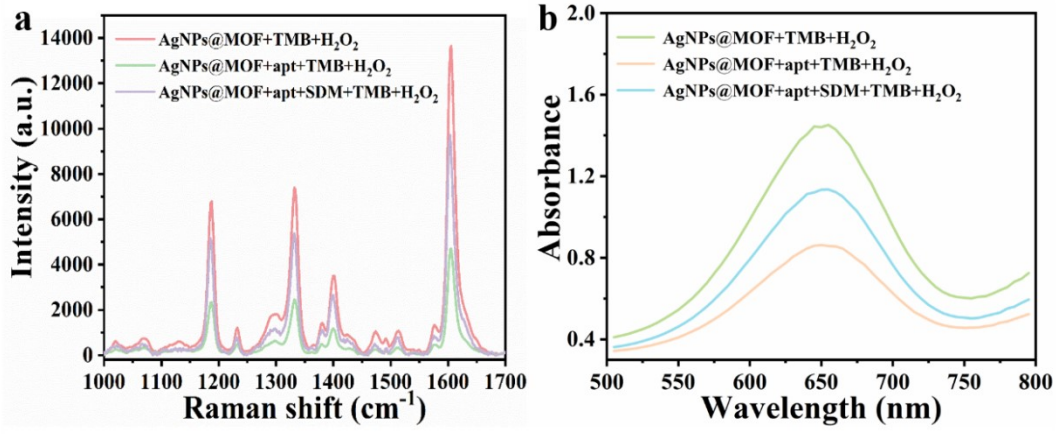

Fig. S2 (a) SERS Spectra and (b) UV-Vis Spectra of TMB solutions of different systems.

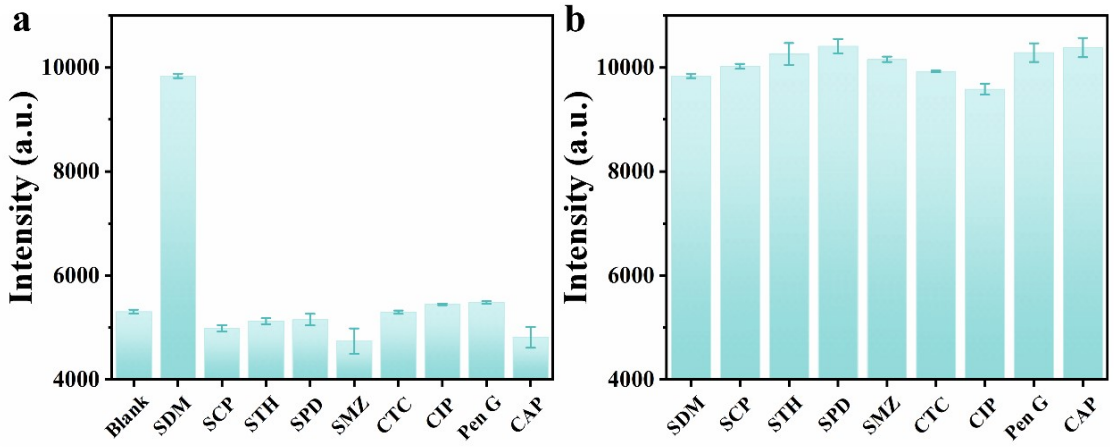

Fig.S3(a) Target selectivity and (b) anti-interference capability of the AgNPs@MOFaptasensor tested against competing antibiotics (200 ng/mL).

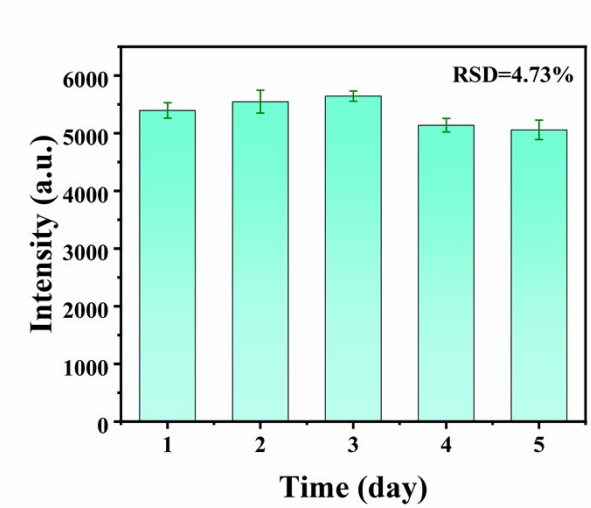

Fig.S4 SERS intensity of AgNPs@MOF composites modified with the same batch of aptamers for oxidizing TMB at different time points

Table S1 Comparison of kinetic parameters between AgNPs@MOF nanozymes and other catalysts

Catalyst	K_m (mM)		v_{max} (10^{-7} Ms^{-1})		Reference
	TMB	H_2O_2	TMB	H_2O_2	
HRP	0.434	3.702	1.000	0.8710	[2]
Fe/Co MOF@Pt	0.351	0.084	8.278	78.860	[3]
MOF-818@ PMOF(Fe)	0.895	0.298	60.100	9.100	[4]

Ag-CDs	0.049	0.287	0.551	0.317	[5]
PCN-Mo@Apt	0.116	0.483	0.893	0.799	[6]
MnO_2	1.410	1.340	0.396	0.775	[7]
PtAg-MoS_2	25.710	0.386	0.729	0.322	[8]
AgNPs@MOF	0.250	0.010	1.810	1.010	This work

Table S2 Comparison of analytic performance of this work with other publications for detecting SDM

Methods	Material	Linear range (ng/mL)	Limit of detection (ng/mL)	Reference
Colorimetric	AuNPs	$10^{-1}\times10^{6}$	10	[9]
Colorimetric	Gr/Ni@Pd	1-500	0.70	[10]
SERS	$CaCO_3$-CuNPs	3×10^{3}-3×10^{5}	1303	[11]
HPLC	-	32-57	40	[12]
CL	AuNPs/Aptamer	0.01-1000	0.004	[13]
Electrochemistry	Au-Mn/rGO	0.001-100	0.00022	[14]
Fluorescence	Gr/Ni@Pd	10-1000	10	[15]
Fluorescence	MSN-NH_2	3-150	2.20	[16]
SERS	AgNPs@MOF	6-200	0.96	This work
Colorimetric	AgNPs@MOF	24-200	2.19	This work

References

[1] Z. Jiang, P. Gao, L. Yang, C. Huang, Y. Li, Facile in Situ Synthesis of Silver Nanoparticles on the Surface of Metal–Organic Framework for Ultrasensitive Surface-Enhanced Raman Scattering Detection of Dopamine, Analytical Chemistry 87(24) (2015) 12177-12182.

[2] L. Gao, J. Zhuang, L. Nie, J. Zhang, Y. Zhang, N. Gu, T. Wang, J. Feng, D. Yang, S. Perrett, X. Yan, Intrinsic peroxidase-like activity of ferromagnetic nanoparticles, Nature Nanotechnology 2(9) (2007) 577-583.

[3] N. Duan, Y. Chang, T. Su, X. Zhang, M. Lu, Z. Wang, S. Wu, Generation of a specific aptamer for accurate detection of sarafloxacin based on fluorescent/colorimetric/SERS triple-readout sensor, Biosensors and Bioelectronics 249 (2024).

[4] H. Chai, K. Yu, Y. Zhao, Z. Zhang, S. Wang, C. Huang, X. Zhang, G. Zhang, MOF-On-MOF Dual Enzyme-Mimic Nanozyme with Enhanced Cascade Catalysis for Colorimetric/Chemiluminescent Dual-Mode Aptasensing, Analytical Chemistry 95(28) (2023) 10785-10794.

[5] A. Wang, C. Guan, G. Shan, Y. Chen, C. Wang, Y. Liu, A nanocomposite prepared from silver nanoparticles and carbon dots with peroxidase mimicking activity for colorimetric and SERS-based determination of uric acid, Microchimica Acta 186(9) (2019).

[6] [6] J. Li, X. Yang, Q. Li, D. Yang, Q. Hu, Z. Zhong, Y. Yang, Sensitive colorimetric aptasensor for multiple foodborne pathogens detection based on PCN-Mo peroxidase-like activity, Food Bioscience 59 (2024).

[7] J. Wang, F. Huang, X. Wang, Y. Wan, Y. Xue, N. Cai, W. Chen, F. Yu, Hierarchically structured Fe3O4-doped MnO2 microspheres as an enhanced peroxidase-like catalyst for low limit of detection, Process Biochemistry 83 (2019) 35-43.

[8] S. Cai, Q. Han, C. Qi, Z. Lian, X. Jia, R. Yang, C. Wang, Pt74Ag26nanoparticle-decorated ultrathin MoS2nanosheets as novel peroxidase mimics for highly selective colorimetric detection of H2O2and glucose, Nanoscale 8(6) (2016) 3685-3693.

[9] [9] J. Yan, Y. Huang, C. Zhang, Z. Fang, W. Bai, M. Yan, C. Zhu, A. Chen, Aptamer based photometric assay for the antibiotic sulfadimethoxine based on the inhibition and reactivation of the peroxidase-like activity of gold nanoparticles, Microchimica Acta 184(1) (2016) 59-63.

[10] A. Wang, H. Zhao, X. Chen, B. Tan, Y. Zhang, X. Quan, A colorimetric aptasensor for sulfadimethoxine detection based on peroxidase-like activity of graphene/nickel@palladium hybrids, Analytical Biochemistry 525 (2017) 92-99.

[11] N.E. Markina, E.K. Volkova, A.M. Zakharevich, I.Y. Goryacheva, A.V. Markin, SERS detection of ceftriaxone and sulfadimethoxine using copper nanoparticles temporally protected by porous calcium carbonate, Microchimica Acta 185(10) (2018).

[12] T.M. Primus, S.M. Jojola, S.J. Robinson, J.J. Johnston, Determination of

Sulfadimethoxine Residues in Skunk Serum by HPLC, Journal of Liquid Chromatography & Related Technologies 30(14) (2007) 2095-2102.
[13] Y. Wang, S. Rink, A.J. Baeumner, M. Seidel, Microfluidic flow-injection aptamer-based chemiluminescence platform for sulfadimethoxine detection, Microchimica Acta 189(3) (2022).
[14] C. Yan, Z. Mu, Y. Wu, X. Liao, J. Zhou, L. Bai, New two-dimensional nanocomposites combined with target-induced strategy in an electrochemical aptasensor for sensitive determination of sulfadimethoxine, Microchimica Acta 190(11) (2023).
[15] K.-M. Song, E. Jeong, W. Jeon, H. Jo, C. Ban, A coordination polymer nanobelt (CPNB)-based aptasensor for sulfadimethoxine, Biosensors and Bioelectronics 33(1) (2012) 113-119.
[16] J. Tang, X. Zheng, S. Jiang, M. Cao, S. Wang, Z. Zhou, X. Nie, Y. Fang, T. Le, Dual fluorescent aptasensor for simultanous and quantitative detection of sulfadimethoxine and oxytetracycin residues in animal-derived foods tissues based on mesoporous silica, Frontiers in Nutrition 9 (2022).