

Nanozyme colorimetric sensor array for on-site detection and discrimination of sulfur-containing metal salts based on Au/CeO₂ heterostructure

Yang Song,^a Zhongyuan Gu,^a Hao Wang,^a Xinxin Shi,^b Changchun He,^a Tongxiang Li,^b Yan Chen,^{*a} Zhao Li^{*a} and Lin Tian,^{*a,b}

^a *School of Materials and Chemical Engineering, Xuzhou University of Technology, XuZhou 221018, PR China*

^b *School of Food (Biology) Engineering, Xuzhou University of Technology, XuZhou 221018, PR China*

Corresponding author: Tel: 86-516-83105518

Email: xzittl@xzit.edu.cn (L. Tian); litx@xzit.edu.cn (T. Li); xzitlz@xzit.edu.cn (Z. Li)

1 Experimental section

1.1 Chemicals and Instrumentation

Cerium nitrate hexahydrate (Ce(NO₃)₂·6H₂O, 99%), ammonium bicarbonate (NH₄HCO₃, 99%), gold chloride trihydrate (HAuCl₄·3H₂O, 99.9%), sodium sulfide (Na₂S, 95%), sodium sulfite (Na₂SO₃, 98%), sodium persulfate (Na₂S₂O₈, 99%), 3,3',5,5'-tetramethylbenzidine (TMB, 98%) were purchased from Shanghai Aladdin Technology Co., Ltd. (Shanghai, China). Acetate buffer (HAc-NaAc) solutions (0.1 M) with different pH values were prepared by HAc and NaAc in distilled water. A 96-well polystyrene plate was obtained from Jincanhua (Shenzhen, China). The other reagents were all analytical grade and used without further purification.

The crystal phase of the obtained samples was established on X-ray powder diffractometer (XRD, UIV, Rigaku). The microstructures and morphologies were acquired by operating a scanning electron microscope (SEM, XL30-ESEM, Philips) and transmission electron microscope (TEM, JEM-2100, JEOL). The chemical composition and elemental valence of products were explored on a X-ray photoelectron spectroscopy spectra (XPS, JPS-9010 MC, JEOL). UV-Vis absorbance spectra were obtained from 200 nm to 1000 nm wavelength using a Shimadzu UV-1900 spectrophotometer.

1.2 Preparation of Au NPs

20 mL of 0.01% HAuCl_4 solution was heat to boiling in a 50 mL round-bottomed. 2 mL of 1% sodium citrate solution was added under vigorous stirring. Then the mixture was refluxed under intense stirring for 10 minutes. After the heating is stopped, the reaction solution was continued stirring for an additional 15 min. Then cooling to room temperature, the Au NPs solution was obtained.

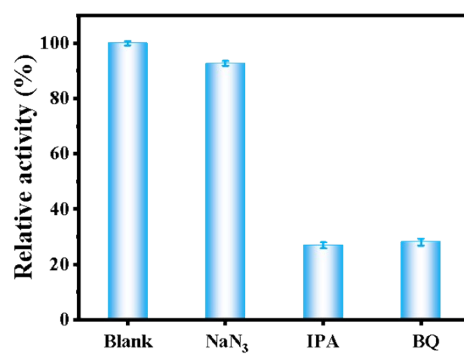


Fig. S1 The effect of NaN₃, IPA and BQ on the peroxidase-like activity

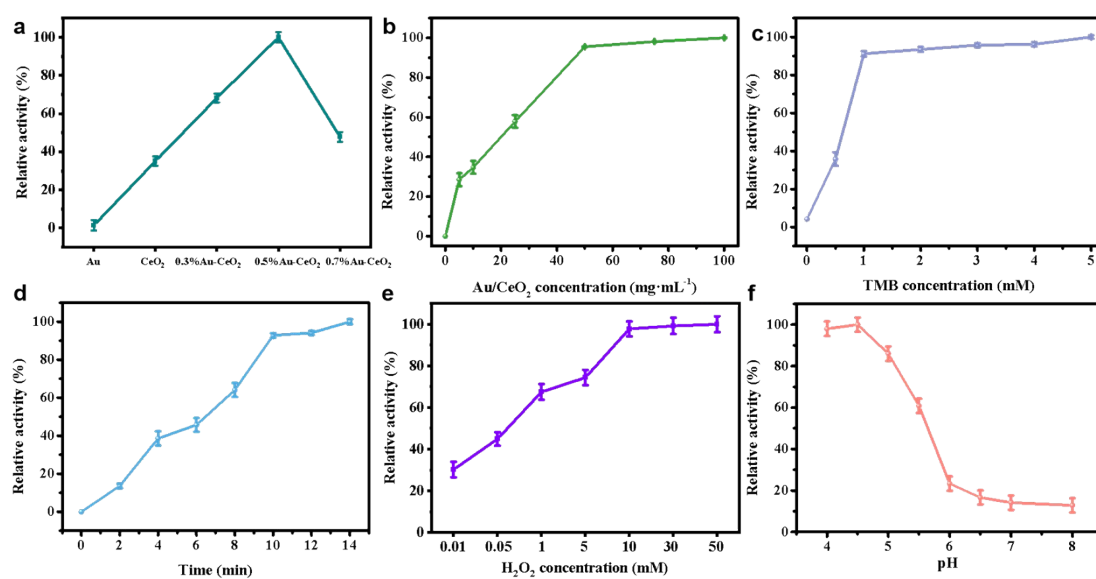


Fig. S2 Dependences of the peroxidase activity of Au/CeO₂ on (a) pH, (b) concentration of Au/CeO₂, (c) concentration of TMB, and (d) time.

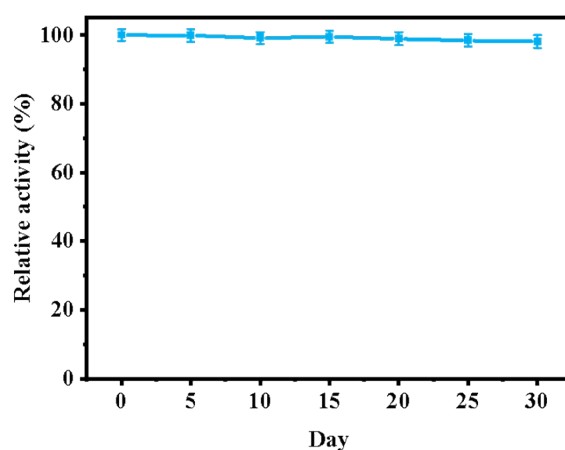


Fig. S3 Stability of Au/CeO₂ at different time.

Table S1 The comparison of the developed colorimetric sensor array with other methods for SCMs.

Methods	Materials	Linear	Detection	References
		range (μM)	limit (μM)	
Fluorescence	AgNF@dsDNA	1-10	0.53	[1]
Fluorescence	FL-H ₂ S	1-13	0.74	[2]
Fluorescence	CyO-DNP	0-50	0.34	[3]
Electrochemistry	Ammineruthenium(III)	0.5-10	0.17	[4]
Colorimetry	Fe-PPOP	80-300	1.1	[5]
Colorimetry	Au/AgI	uncertain	40	[6]
Fluorescence	BTN	0-40	1.01	[7]
Colorimetry	CuNPs	12.5-50	8.1	[8]
Colorimetric sensor array	Au/CeO ₂	5-110	4.7	This work

AgNF@dsDNA: double-strand DNA (dsDNA)-stabilized silver nanoflakes

DNP: 2, 4-dinitrophenyl

Fe-PPOP: iron porphyrin-based porous organic polymer

References:

1. S.T. Xie, T. Fu, L. He, L.P. Qiu, H.L. Liu, *Anal. Chem.*, 2019, **91**, 15404-15410.

2. D.H. Ding, J.F. Li, L.Z. Xu, J.Y. Wang, D. Tan, W.Y. Lin, *J. Mater. Chem. B.*, 2022, **10**, 4568-4574.
3. Z.P. She, W.X. Wang, W.L. Jiang, Z.Q. Wang, G.J. Mao, J.J. Fei, Y.F. Li, C.Y. Li, *Anal. Chem.*, 2021, **93**, 11826-11835.
4. S.J. Wang, X.M. Liu, M.N. Zhang, *Anal. Chem.*, 2017, **89**, 5382-5388.
5. L.H. Liao, D. Guo, X.G. Luo, L.K. Meng, F.S. Wu, *Colloid. Surface. A Physicochem. Eng. Aspects*, 2022, **651**, 129727.
6. J. Zeng, M. Li, A. Liu, F. Feng, T. Zeng, W. Duan, M.Li, M. Gong, C.Y. Wen, Y. Yin, *Adv. Funct. Mater.*, 2018, **28**, 1800515.
7. Q. Chen, P. Xing, Y. Xu, H. Li, S. Sun, *Chinese J. Chem.*, 2017, **35**, 477-482.
8. A. Hatamie, B. Zargar, A. Jalali, *Talanta*, 2014, **121**, 234-238.

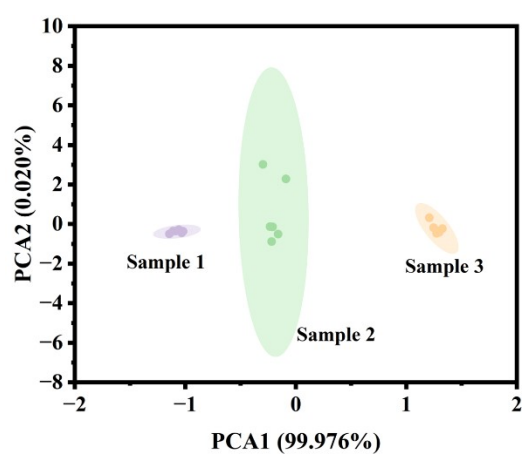


Fig. S4 PCA diagram of the sensor array in the environmental samples.