Supporting Information

Molecule-gated surface chemistry of Pt nanoparticles for constructing

activity-controllable nanozyme and a three-in-one sensor

Min Gao,[‡]^a Pengli An,[‡]^a Honghong Rao,^b Zhengrong Niu,^a Xin Xue,^a Mingyue Luo,^c Xiuhui Liu,^a Zhonghua Xue^{a*} and Xiaoquan Lu^{a*}

^a Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou, 730070 (China)

^b School of Chemistry & Chemical Engineering, Lanzhou City University, Lanzhou, 730070 (China)

^c College of Geography and Environment Science, Northwest Normal University, Lanzhou, 730070 (China).

‡ These authors contributed equally to this work.

*Corresponding author. Tel.: Fax: +86 0931 7970520. E-mail address: xzh@nwnu.edu.cn and luxq@nwnu.edu.c



Fig. S1 (A) The size distribution histogram and (B) TEM image of PtNPs (the scale bar: 20 nm). (C) XPS survey spectrum of PtNPs.



Fig. S2 (A) Vis absorption spectra of (a) TMB, (b) TMB-PtNPs in air-saturated solution, and (c) TMB-PtNPs in N_2 -saturated solution. (B) Vis absorption spectra of (a) ABTS, (b) ABTS-PtNPs in air-saturated solution, and (c) ABTS-PtNPs in N_2 -saturated solution. (C) Fluorescence spectra of (a) OPD, (b) OPD-PtNPs in-air saturated solution, and (c) OPD-PtNPs in N_2 -saturated solution. Insert: the corresponding photographs.



Fig. S3 (A) Michaelis-Menten curve of PtNPs as oxidase mimics. (B) Lineweaver-Burk linear plot of PtNPs as oxidase mimics in 0.2 M NaAc-HAc buffer solution (pH 4.0) with the addition of different concentration TMB.



Fig. S4 (A) The Vis absorption spectra of TMB after incubation with PtNPs in the presence of specific scavengers. (B) The corresponding bar diagram.



Fig. S5 (A) TEM image of GSH@PtNPs (the scale bar: 50 nm). (B) The XPS survey spectrum of GSH@PtNPs. (C) XPS spectrum of S(2p) in GSH@PtNPs.



Fig. S6 Time-evolution of the absorbance of TMB solution at 652 nm after incubation with PtNPs (30 μ L) at different pH conditions: (a) pH 2.0, (b) pH 3.0, (c) pH 4.0, (d) pH 5.0, (e) pH 6.0, (f) pH 7.0, and (g) pH 8.0, respectively.



Fig. S7 (A) Vis absorption spectra of different concentration of TMB (0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mM) after incubation with PtNPs (30 μ L) at room temperature; (B) Plot of corresponding absorbance at 652 nm versus the concentration of TMB.



Fig. S8 (A) Vis absorption spectra of TMB (0.4 mM) under different amounts of PtNPs (5 μ L, 10 μ L, 15 μ L, 20 μ L, 25 μ L, 30 μ L, 35 μ L, 40 μ L, 45 μ L) at room temperature, respectively; (B) Plot of corresponding absorption at 652 nm versus the volume of PtNPs.



Fig. S9 (A) Vis absorption spectra of the solution containing TMB (0.4 mM) and Pt NPs (30μ L) under different concentrations of GSH (0, 2.5, 5, 10, 15, 20, 30, 40, 50, 80, 100, 150, 200, 300 μ M) at room temperature, respectively; (B) Plot of corresponding absorption at 652 nm versus the GSH concentration.



Fig. S10 The effect of different pH conditions between Cu^{2+} and GSH on the TMB oxidation (a-i: 4.0-12.0, respectively). (A) The Vis absorption spectra of TMB under different pH and (B) the plot of corresponding absorbance at 652 nm vs pH.



Fig. S11 The effect of different incubation time between Cu²⁺ and GSH on the TMB oxidation (a-f: 0, 10, 20, 30, 40, 50 min). (A) Vis absorption spectra of TMB under different incubation time points and (B) the plot of corresponding absorbance at 652 nm vs time.



Fig. S12 (A) Temperature monitoring of different components in colorimetric reaction solutions during the 808 nm laser irradiation for 600 s and (B) the relationship between temperature and irradiation time (0-100 s).



Fig. S13 (A) Absorption spectra of GSH at 50 °C for 20 min (pH 4.0) (a), GSH + Cu²⁺ at room temperature for 20 min (pH 4.0) (b), GSH + Cu²⁺ at 50 °C (c) for 20 min (pH 4.0), GSH at 50 °C for 20 min (pH 10.0) (d), GSH + Cu²⁺ at room temperature (e), and GSH + Cu²⁺ at 50 °C for 20 min (pH 10.0) (f). (B) Absorption spectra of 100 μ M GSH after addition of different concentrations of Cu²⁺ (0 nM, 100 nM, 300 nM, 500 nM, 800 nM). Insert: absorbance at 300 nm as a function of Cu²⁺ concentration.



Fig. S14 Mass spectrum (MS) of 100 μ M GSH after incubation with Cu²⁺ (0.8 μ M). (Reaction conditions: incubation temperature 50 °C, incubation time 20 min, pH 10.0.)



Fig. S15 The UV-vis absorption (a), fluorescence excitation (b), and emission (c) spectra of TMB (0.4 mM) and emission spectra of TMB-PtNPs (d) in 0.2 M NaAc-HAc buffer solution (pH 4.0). Insert a_1 - c_1 : the TMB solution in the visible light, the TMB solution in the ultraviolet lamp (b₁), and the TMB-PtNPs solution in the ultraviolet lamp (c₁),respectively.



Fig. S16 Temperature increments (ΔT) of different components in colorimetric reaction solutions during an 808 nm laser irradiation at a 4.5 W for 100 s at different room temperature.



Fig. S17 Selectivity of the three-in-one assay for Cu^{2+} . (A) Vis absorption spectra, (C) temperature change after irradiation with an 808 nm during 100 s, and (E) fluorescence spectra of TMB-PtNPs-GSH reaction system in the presence of different anions. (B, D, and F) the corresponding histogram.

Catalyst	Substrate	<i>K</i> _m (mM)	V _{max} (10 ⁻⁸ M/s)	Reference
ZnFe ₂ O ₄ MNPs	ТМВ	0.85	13.31	1
WS ₂ nanosheets	ТМВ	1.83	4.31	2
HRP	ТМВ	0.43	10.00	3
PtNPs	ТМВ	0.062	11.44	This work

Table S1 Apparent steady-state kinetics parameters of PtNPs and other nanomaterialoxidase mimics.

 $\mathcal{E}_{\text{TMBox}}$ = 39000 M⁻¹ ·cm⁻¹, b = 1 cm

Detection Methods	Probes	Linear Range	LOD	Ref.
Atomic absorption	Methylthymol blue complexes	5-40 ng mL ⁻¹	0.54 ng mL ⁻¹	4
Atomic absorption	Ammonium nitrate	-	0.06 ppb	5
Electrochemical	Functionalized polypyrrole nanotube	0.1–30 μM	46 nM	6
Colorimetric	Cys-AuNR	1.0-100 μM	0.34 μM	7
Colorimetric	Starch-AgNPs	0.1-10 μM	0.632 μM	8
Fluorimetric	BSA-ZnO NPs	0.50-10 μM	0.61 μM	9
Fluorimetric	Au NCs	0.5-70 μM	0.38 μM	10
Colorimetric		50-800 nM	7.0 nM	This
Photothermal	GSH@PtNPs	50-600 nM	38.3 nM	INIS
Fluorimetric		25-300 nM	6.8 nM	WORK

Table S2Performance comparison of different assays for Cu²⁺ detection.

Reference

- 1. L. Su, J. Feng, X. Zhou, C. Ren, H. Li and X. Chen, Anal. Chem., 2012, 84, 5753-5758.
- T. Lin, L. Zhong, Z. Song, L. Guo, H. Wu, Q. Guo, Y. Chen, F. Fu and G. Chen, *Biosens*. *Bioelectron*, 2014, 62, 302-307.
- G. Lizeng, Z. Jie, N. Leng, Z. Jinbin, Z. Yu, G. Ning, W. Taihong, F. Jing, Y. Dongling and P. Sarah, *Nature Nanotech.*, 2007, 2, 577-583.
- 4. N. Pourreza and R. Hoveizavi, Anal. Chim. Acta, 2005, 549, 124-128.
- 5. M. S. Chan and S. D. Huang, *Talanta*, 2000, **51**, 373-380.
- 6. M. Lin, X. Hu, Z. Ma and L. Chen, Anal. Chim. Acta, 2012, 746, 63-69.
- 7. J. M. Liu, H. F. Wang and X. P. Yan, *Analyst*, 2011, **136**, 3904-3910.
- L.-J. Miao, J.-W. Xin, Z.-Y. Shen, Y.-J. Zhang, H.-Y. Wang and A.-G. Wu, Sens. Actuators B Chem., 2013, 176, 906-912.
- 9. Z. Chen and D. Wu, Sens. Actuators B Chem., 2014, 192, 83-91.
- S. Chen, Y. Kuang, P. Zhang, Y. Huang, A. Wen, X. Zeng, R. Feng, H. Nie, X. Jiang and Y. Long, Sens. Actuators B Chem., 2017, 253, 283-291.