Supporting information

Hemin-functionalized WS_2 nanosheets as highly active peroxidase mimetic for label-free colorimetric detections of H_2O_2 and glucose

Qiao Chen^{ab}, Jia Chen^a, Cunji Gao^a, Mingliang Zhang^a, Junying Chen^b and Hongdeng Qiu^{*a}

a Key Laboratory of Chemistry of Northwestern Plant Resources, Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China. E-mail: hdqiu@licp.cas.cn (H. Qiu); b School of Materials Science and Engineering, Key Laboratory for Advanced Technologies of

Materials of the Ministry of Education, Southwest Jiaotong University, Chengdu 610031, China.



Fig. S1. TEM image (A), SAED pattern (B), High-resolution TEM image (C), (D) of the WS_2 nanosheets.



Fig. S2. SEM images of WS_2 nanosheets (A) and hemin/ WS_2 -NSs (B).



Fig. S3. The color changing with the increasing of reaction time after mixing hemin/WS₂-NSs (3.2 μ g mL⁻¹) with TMB (1.0 mmol L⁻¹) and H₂O₂ (0.08 mmol L⁻¹) in a reaction volume of 1.0 mL HAc-NaAc buffer (0.2 mmol L⁻¹, pH 4.0).

Fig. S4. The catalytic activity with hemin, WS_2 -NSs and hemin/ WS_2 -NSs at the different concentrations of H_2O_2 .



Fig. S5. (A) Photos of oxidation of OPD (20 mM) in HAc-NaAc buffer (0.2 mM, pH 4.0) at room temperature for 30 min in the presence of $3.2 \ \mu\text{g/mL}$ hemin/WS₂-NSs (a), 1.0 mM H₂O₂ (b), and 1.0 mM H₂O₂ + 3.2 μ g/mL hemin/WS₂-NSs (c); (B) Photos of oxidation of ABTS (10 mM) in HAc-NaAc buffer (0.2 mM, pH 4.0) at room temperature for 30 min in the presence of $3.2 \ \mu\text{g/mL}$ hemin/WS₂-NSs (a), 1.0 mM H₂O₂ (b), and 1.0 mM H₂O₂ + 3.2 μ g/mL hemin/WS₂-NSs (a), 1.0 mM



Fig. S6. Effect of reaction time (A), pH (B), temperature (C), and H_2O_2 concentration (D) on the peroxidase-like activity of hemin/WS₂-NSs for the TMB oxidation. The experiment was carried out using 3.2 µg mL⁻¹ hemin/WS₂-NSs in a reaction volume of 1.0 mL, in HAc-NaAc buffer (0.2 mM, pH 4.0) with 1.0 mM TMB and 0.08 mM H_2O_2 for 30 min at 40 °C. The error bars represent the standard deviation of three measurements.

Fig. S7. Selectivity analysis for glucose detection by monitoring the relative absorbance. The error bars represent the standard deviation of three measurements.

Table S1. Comparison of the apparent Michaelies-Menten constant (Km) and maximum reaction rate (Vmax) between hemin/WS₂-NSs and others. Km is the Michaelies constant, Vmax is the maximal reaction velocity.

Catalyst	substance	Km (mM)	Vmax (M/s)
Hemin-functionalized	H_2O_2	0.926	2.75×10-8
WS ₂ nanosheets	TMB	0.467	6.45×10 ⁻⁸
HRP	H_2O_2	3.70	8.71×10 ⁻⁸
	TMB	0.434	10.00×10-8
WS ₂ -NSs	H ₂ O ₂	0.24	4.52×10 ⁻⁸
	TMB	1.83	4.31×10 ⁻⁸
Hemin	H ₂ O ₂	2.74	3.53×10-8
	TMB	4.84	4.69×10 ⁻⁸

Table S2. A list of a series of H_2O_2 and glucose sensors based on nanomaterials owning peroxidase-like activity.

Catalyst	Method	Linear range	LOD	Ref
		(µM)	(µM)	
Co ₃ O ₄ NPs	Electrochemical	50-25000	10	[S1]
Hemin@MOF ¹	Colorimetric	5-200	2	[S2]
Fe ₃ O ₄ MNPs	Colorimetric	5-100	3	[83]
Fe ₃ O ₄ MNPs	Electrochemical	4.2-800	1.4	[S4]
WS_2	Colorimetric	10-100	1.2	[85]
Hemin/WS ₂ -NSs	Colorimetric	5-140	1.0	This work

$^{a)}\,H_2O_2$ detection with peroxidase mimic

^{b)}Glucose detection with peroxidase mimic

Catalyst	Method	Linear range	LOD	Ref
		(µM)	(µM)	
Co ₃ O ₄ NPs	Electrochemical	10-1000	5	[S2]
Hemin@MOF1	Colorimetric	10-300	Not given	[83]
Fe ₃ O ₄ MNPs	Colorimetric	50-1000	30	[S4]
WS_2	Colorimetric	5-300	2.9	[85]
Hemin/WS ₂ -NSs	Colorimetric	5-200	1.5	This work

¹MOF: metal-organic framework.

Foreign substance	Concentration	Chang in absorption signal
	(mM)	(%) ^a
KCl	500	4.1
NaCl	500	4.7
CaCl ₂	200	5.9
Dopamine	30	4.4
Cysteine	10	4.1
Ascorbic acid	10	3.9
ClO-	0.5	2.7
$Cr_2O_7^{2-}$	0.5	3.1

Table S3. Influence of foreign substances on the detection of 10 μM H_2O_2 using the proposed sensor.

^a The average value of five experiments

Sample	Added	Found	Recovery	RSD
number	(mmol L ⁻¹)	(mmol L ⁻¹)	(%)	(%,n=5)
1	10.0	9.9	99.0	2.8
2	10.0	10.2	102.0	1.6
3	10.0	9.7	97.0	4.0

Table S4. Results of the determination of glucose in human serum samples.

References:

- [S1] J. Mu, Y. Wang, M. Zhao and L. Zhang, Chem. Commun., 2012, 48, 2540–2542.
- [S2] F. X. Qin, S. Y. Jia, F. F. Wang, S. H. Wu, J. Song and Y. Liu, *Catal. Sci. Technol.*, 2013, 3, 2761-2768.
- [S3] H. Wei and E. Wang, Anal. Chem., 2008, 80, 2250-2254.
- [S4] L. Zhang, Y. Zhai, N. Gao, D. Wen and S. Dong, *Electrochem. Commun.*, 2008, 10, 1524–1526.
- [S5] 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.