Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.
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Supporting Information

Protein-mediated wool-ball-like copper sulfide as multifunctional nanozyme for dual fluorescence "turn-on" sensors of cysteine and silver ion

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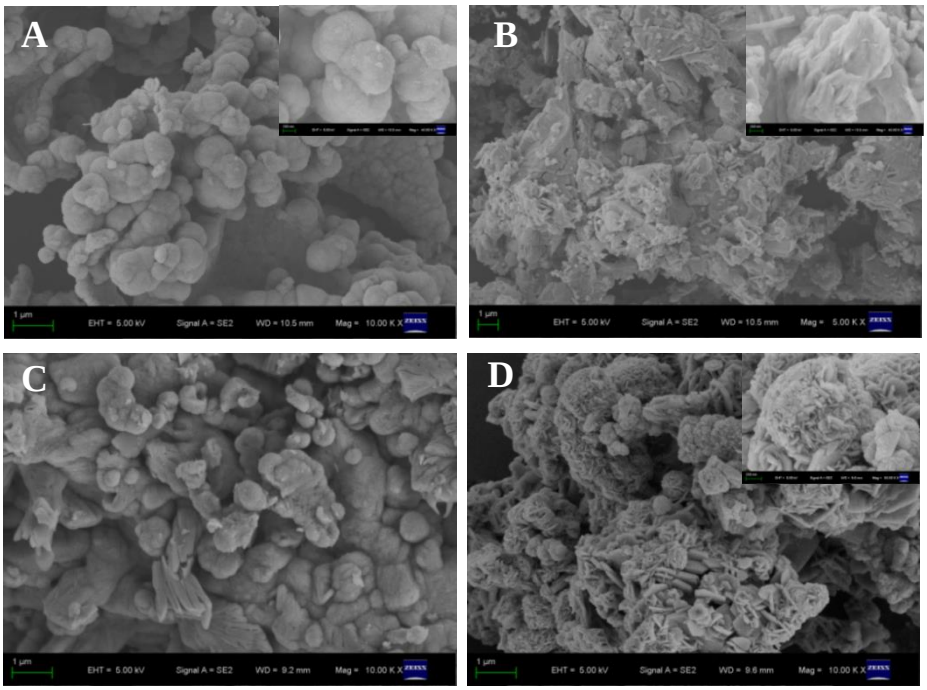

Fig. S1. SEM images of copper sulfide prepared in the presence of different biomolecules: aspartic acid (A), histidine (B), hydrolyzed casein (C) and no additive (D).

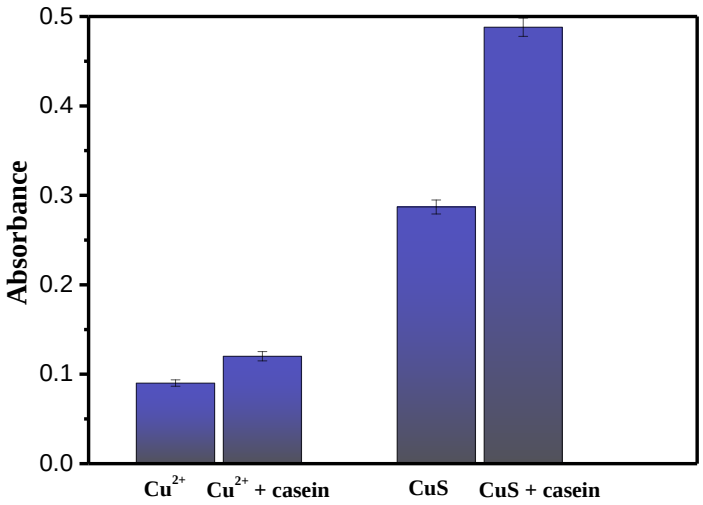

Fig. S2. The absorbance at 625nm of the TMB and H_2O_2 mixture in different systems.

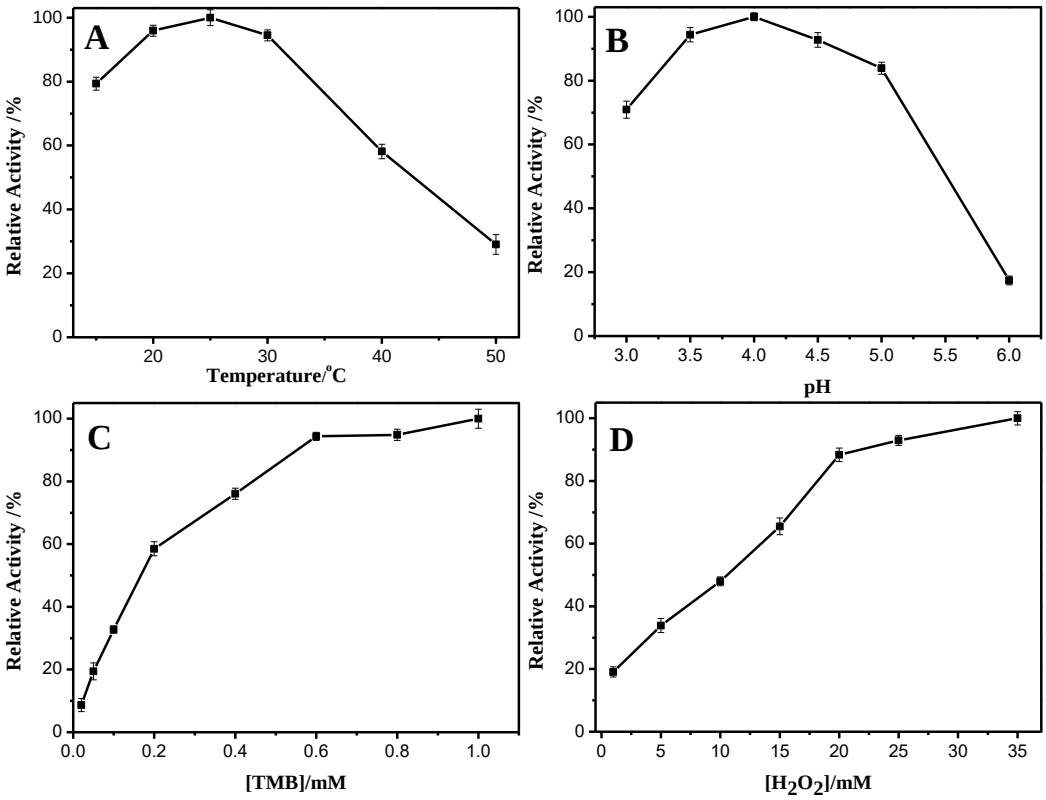

Fig. S3. Effects of (A) temperature, (B) pH, (C) TMB concentration, and (D) H_2O_2 concentration on the peroxidase-like activity of WBLCS.

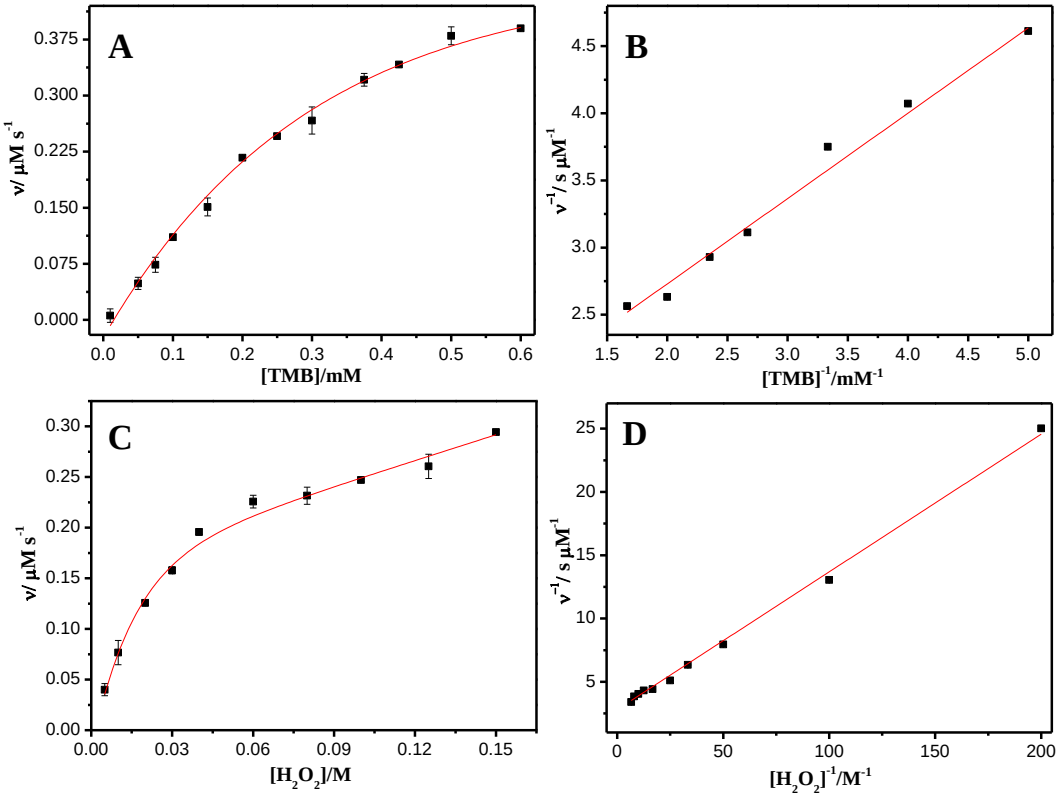

Fig. S4. Correlation of initial reaction velocity with different concentrations of (A) TMB and (C) H_2O_2. (B, D) The double-reciprocal plots of (A) and (C), respectively.

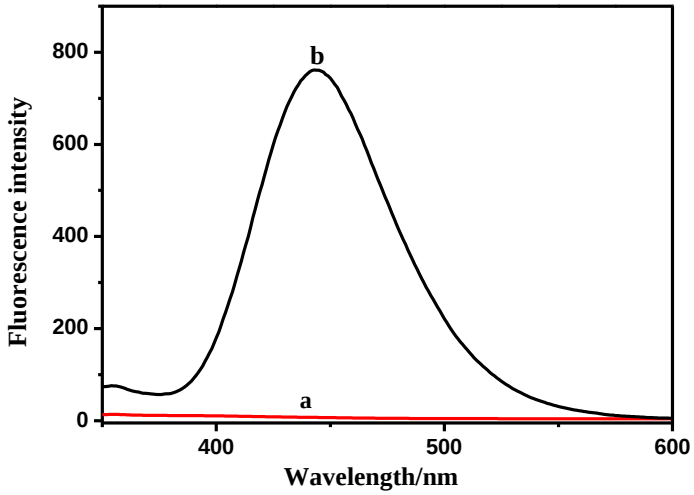

Fig. S5. Fluorescence spectra of different systems (a: WBLCS + TA, b: WBLCS + TA + H_2O_2). ([TA]=0.25 mM, [H_2O_2]=1 mM)

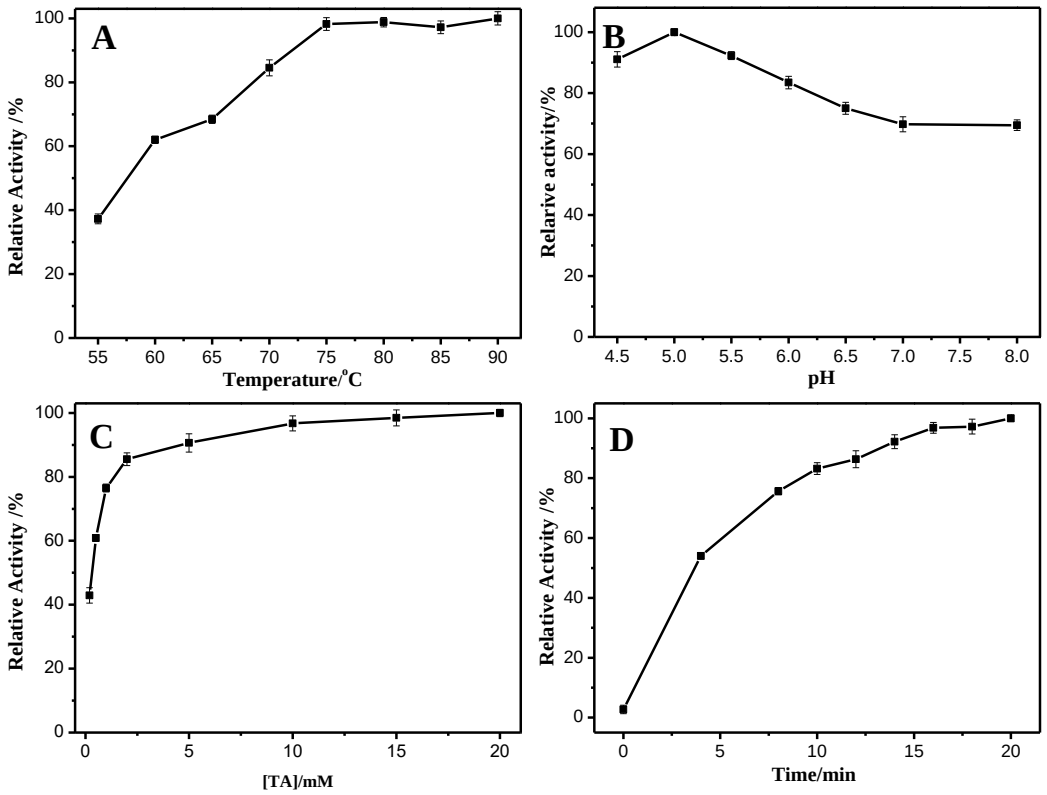

Fig. S6. Effect of (A) temperature, (B) pH, (C) TA concentration and (D) reaction time on the cascade performance of WBLCS.

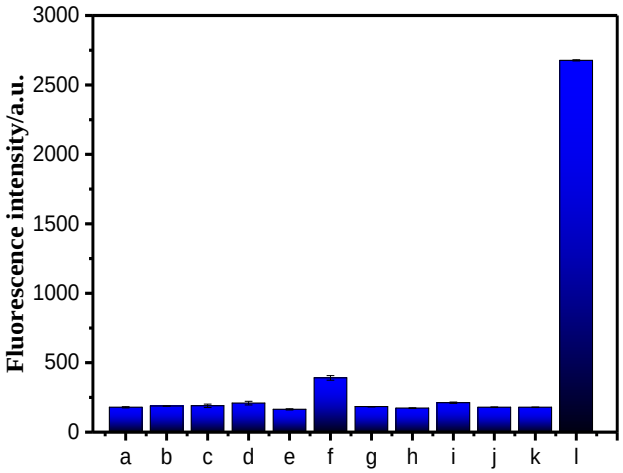

Fig. S7. Fluorescence intensity of WBLCS-TA system in the presence of different biomolecules. (a) proline, (b) aspartic acid, (c) GSH, (d) glucose, (e) fructose, (f) lactose, (g) histidine, (h) arginine, (i) methionine, (j) tyrosine, (k) lysine, (l) cysteine ([Cys] = 0.1 mM, concentration of other substances being 1.25 mM).

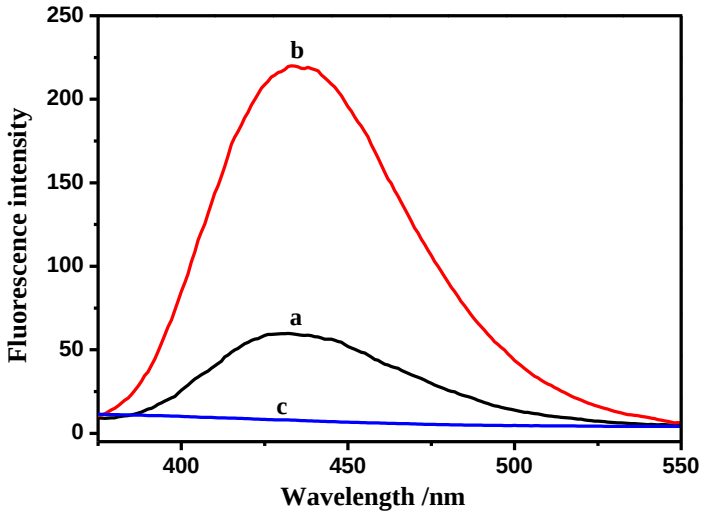

Fig. S8. The fluorescence spectra of different systems, a: WBLCS + TA + Cys, b: WBLCS + TA + Cys + Ag^{+}, c: TA+ Cys + Ag^{+}. ([TA]=0.025 mM, [Cys]=0.5 mM)

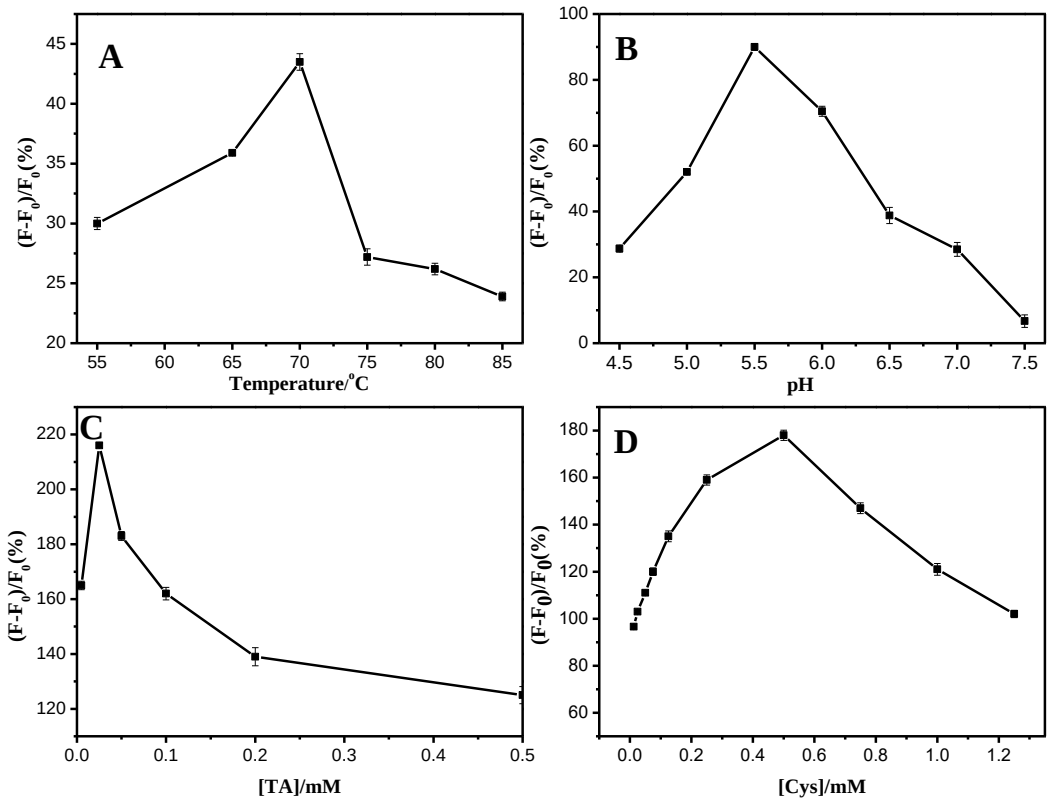

Fig. S9. Effect of (A) temperature, (B) pH, (C) TA concentration and (D) Cys concentration on the fluorescence intensity change of WBLCS-TA -Cys systems with and without silver ions.

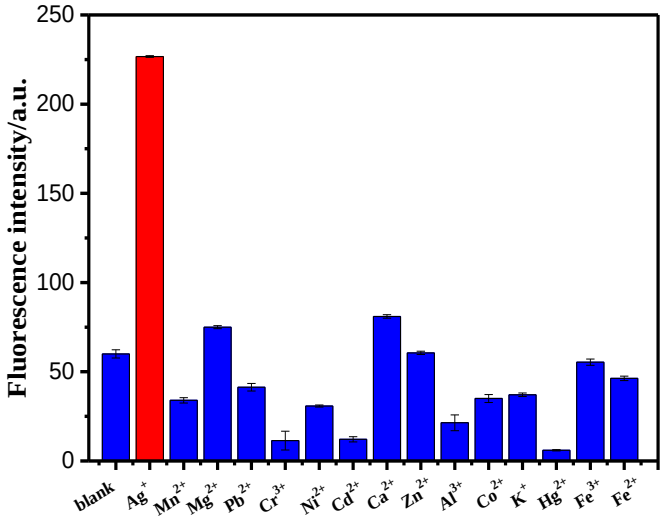

Fig. S10. Fluorescence intensity of WBLCS-TA-Cys system in the presence of different metal ions ([Ag^{+}]=0.075 mM, other ion concentration being 0.5 mM)

Table S1. Comparison of the apparent Michaelis-Menton constant (K_m) and maximum reaction rate (V_{max}) of WBLCS.

Enzyme	K_m (mM)		V_{max} (10^{-8} M s^{-1})		Reference
	TMB	H_2O_2	TMB	H_2O_2	
HRP	0.434	3.7	10.0	8.71	1
Bare CuS	0.11	101.8	0.038	0.043	2
CuS-Asp0.05	0.09	103.2	33.1	38.2	2
Hollow-CuS NCs	1.62	0.94	16.64	2.55	3
CuS-BSA-$Cu_3(PO_4)_2$	0.55	0.29	8.2	8.31	4
50Co/CuS-MMT	0.077	3.422	10.373	7.054	5
WBLCS	0.435	0.04	68.5	35.6	This work

Table S2. Comparison of different methods for cysteine detection based on nanozymes.

Method	Linear range (μM)	Detection limit	Sensing systems	Mode	Reference
Colorimetric	25-300	11.26 μM	$CuMnO_2$-TMB-H_2O_2	Turn off	6
Colorimetric	1-20	150 nM	FeCoNPs-TMB-H_2O_2	Turn off	7
Colorimetric	1-10	80 nM	MoS_2-PPy-Pd -TMB-H_2O_2	Turn off	8
Colorimetric	0.05-10	24.2 nM	Mo^{6+}- Co_3O_4-TMB-H_2O_2	Turn off	9
Fluorescence	0.63-100	6.6 nM	CuONPs-TA	Turn on	10
Fluorescence	0.03-125	1.0 nM	WBLCS-TA	Turn on	This work

Table S3. Determination of cysteine in serum sample using the proposed method.

Added (μM)	Found (μM)	Recovery (%)	RSD (%, n=3)
0.00	0.23	—	3.1
0.50	0.75	104.0	2.2
3.00	3.18	98.3	1.4
10.00	10.35	101.2	3.3

Table S4. Comparison of different methods for Ag^+ detection.

Method	Linear range	Detection limit (nM)	Sensing systems	Mode	Reference
Colorimetric	30-300 nM	4.7	His–PdNPs-TMB-H_2O_2	Turn off	11
Colorimetric	0.5 -10 μM	204	BSA@AuNCs-TMB-H_2O_2	Turn off	12
Colorimetric	0.1-8.0 μM	10	Casein-Au- TMB-H_2O_2	Turn off	13
Colorimetric	2-5 nM	1.43	Citrate-ZIF-8/GO-TMB-H_2O_2	Turn on	14
Fluorescence	0.1 -4 μM	50	CDs/AuNP	blue-red-blue	15
Fluorescence	5 nM-0.05 μM	5	Si-CDs@DA	Turn off	16
Fluorescence	0. 1 nM-1 μM	0.037	CuONPs-TA-GSH	Turn off	17
Fluorescence	50 nM-75 μM	5	WBLCS-TA-Cys	Turn on	This work

Table S5. Detection of Ag^{+} in real samples using the proposed method.

Sample	Added (μM)	Found (μM)	Recovery (%)	RSD (%, n=3)
Serum	1.0	0.98	98.4	2.0
	2.0	1.98	99.2	1.0
	3.0	3.03	100.9	1.2
Lake water	1.0	0.98	97.7	2.8
	2.0	1.97	98.5	2.1
	3.0	3.09	103.2	3.9

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