Supporting information

Three-dimensional network structure of metal-based nanozymes for the construction of colorimetric sensors for the detection of antioxidants

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Materials and Reagents. 4-nitrophthalonitrile (Ark pharm), 4-Hydroxybenzaldehyde (Alfa Aesar), $FeCl_2 \cdot 4H_2O$, $CuAc_2 \cdot H_2O$, $ZnAc_2 \cdot 2H_2O$, 1,8-diazabicyclo[5.4.0]undec-7-ene (Innochem), dimethylaminoethanol (Alfa Aesar), acetone, NaAc, chitosan (Sinopharm Chemical Reagent), graphene oxide powder (JCNO). 3,3′,5,5′-tetramethylbenzidine (TMB), Glutathione (GSH), ascorbic acid (AA), cysteine (Cys), tannin (TA), catechin (C), dopamine (DA), uric acid (UA) were obtained from Sigma-Aldrich, Co-N-C (from laboratory)，H_2O_2，Acetate buffer (HAc-NaAc) solutions (0.2 M) with different pH values were prepared by acetic acid and sodium acetate in distilled water. K_2CO_3, NaOH, N,N-dimethylformamide, absolute ethyl alcohol, and 36 % acetic acid were purchased from Beijing chemical reagent factory. All the chemicals were of analytical pure grade and used as received without further purification.

Instrumentation. The morphologies of the samples were characterized by scanning electron microscopy (SEM, Hitachi, Japan) and transmission electron microscopy (TEM, Hitachi, Japan). The high-resolution TEM (HRTEM) and elemental mappings were obtained from a scanning transmission electron microscope (STEM). The X-ray diffraction (XRD) pattern was performed on a D8 ADVANCE/Bruker diffractometer (Germany) employing the Cu Kα radiation source(λ = 0.1541 nm). X-ray photoelectron spectroscopy (XPS) (ESCALAB 250, UK) was monochromatic Al Kα radiation as the excitation source. Extended X-ray absorption fine structure (EXAFS)-constituted XAFS spectra were acquired at the Beijing Synchrotron Radiation Facility. The absorption spectra of Fe，Cu，Zn K-edge spectra were collected in the fluorescence mode using a double-crystal Si(111) monochromatic. Colorimetric absorbance was measured with UV-2700 spectrophotometer (Daojin, Japan).

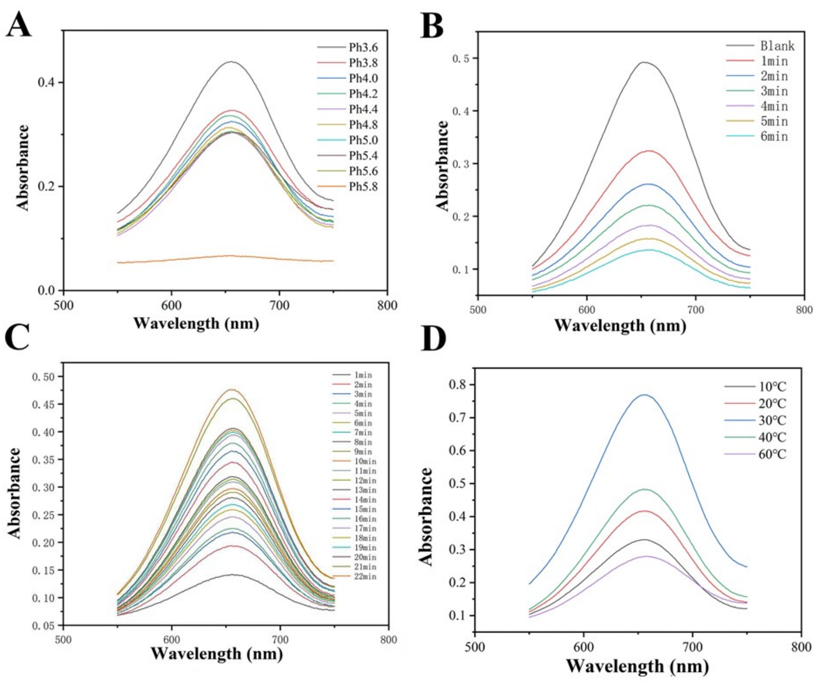

Fig. S1. UV-Vis absorption spectra of oxTMB under different conditions. (A)pH, (B) Antioxidant action time, (C) Reaction time, (D) Reaction temperature. Fe-based nanozyme.

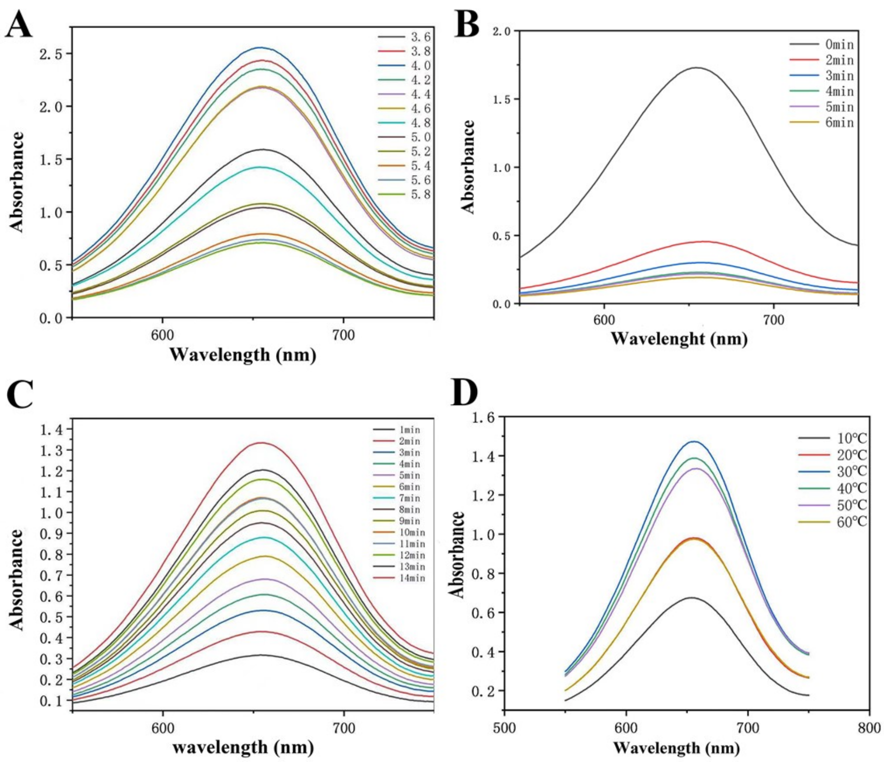

Fig. S2. UV-Vis absorption spectra of oxTMB under different conditions. (A)pH, (B) Antioxidant action time, (C) Reaction time, (D) Reaction temperature. Cu-based nanozyme.

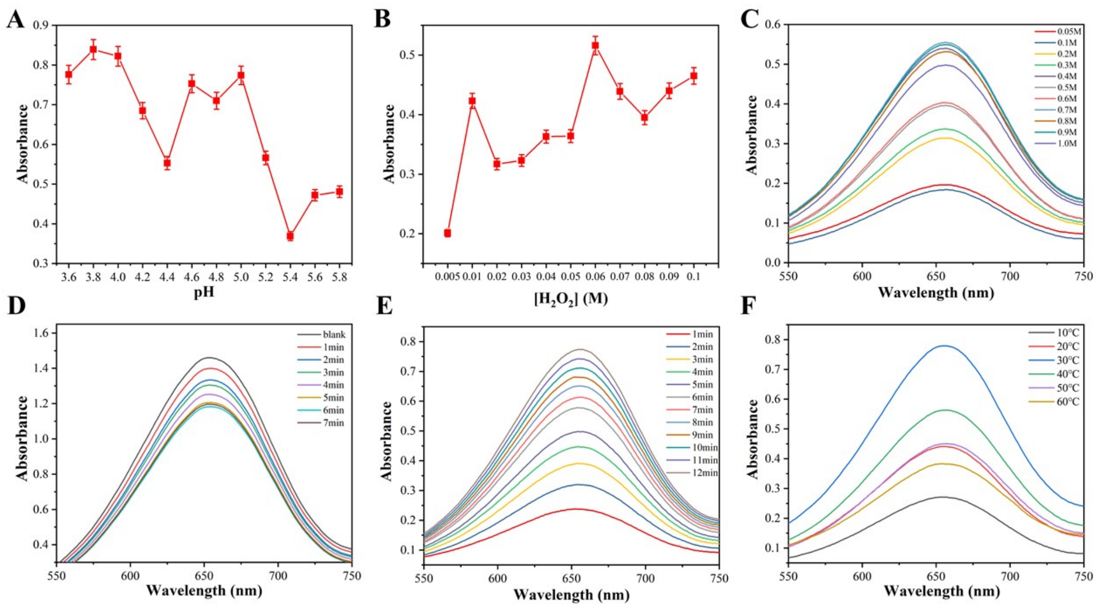

Fig. S3. UV-Vis absorption spectra of oxTMB under different conditions. (A)pH, (B)H_2O_2 concentration, (C)TMB concentration, (D) Antioxidant action time, (E) Reaction time, (F) Reaction temperature. Zn-based nanozyme.

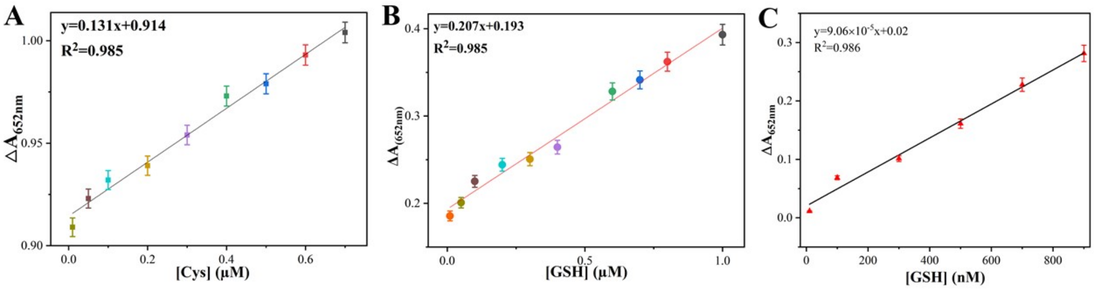

Fig. S4. The linear relationships of Cys and GSH in Cu-based nanozyme (A), Fe-based nanozyme (B), Zn-based nanozyme (C).

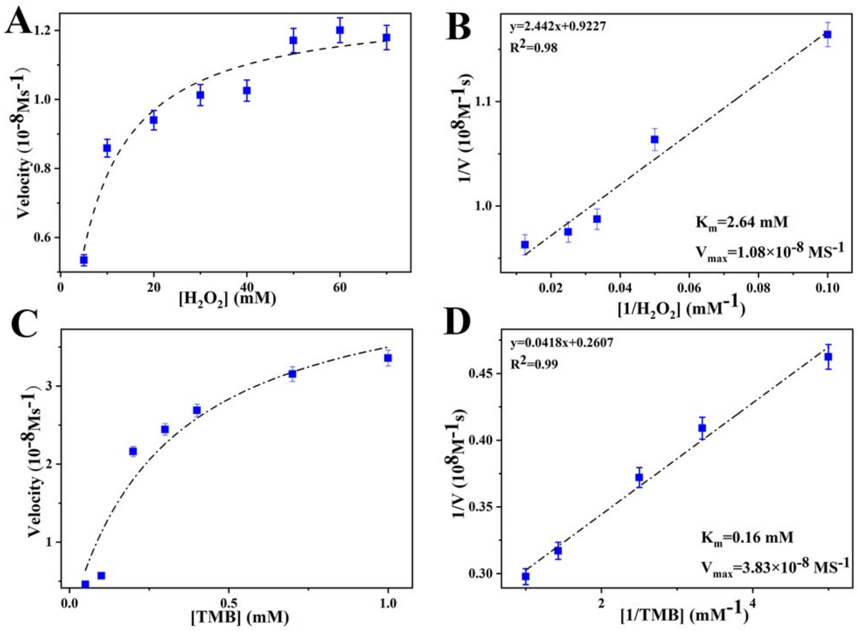

Fig. S5. (A)Reaction rate curve, (B)double reciprocal curve of reaction rate and substrate concentration of Co-based nanozyme, using H_2O_2 as a substrate. (C)Reaction rate curve, (D)double reciprocal curve of reaction rate and substrate concentration of Co-based nanozyme. Using TMB as a substrate.

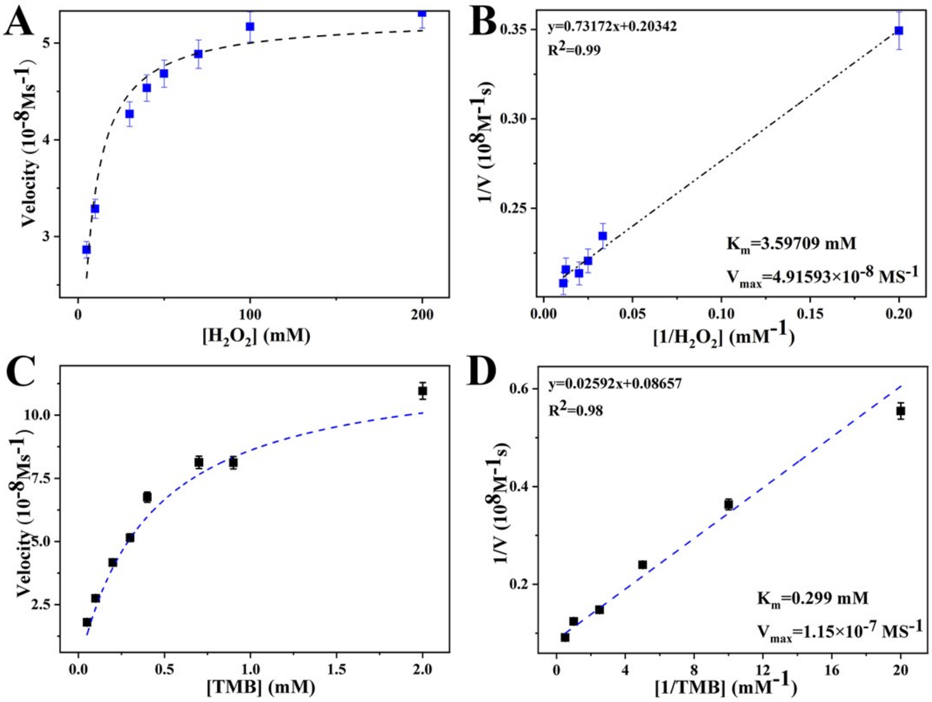

Fig. S6. (A)Reaction rate curve, (B)double reciprocal curve of reaction rate and substrate concentration of Cu-based nanozyme, using H_2O_2 as a substrate. (C)Reaction rate curve, (D)double reciprocal curve of reaction rate and substrate concentration of Cu-based nanozyme. Using TMB as a substrate.

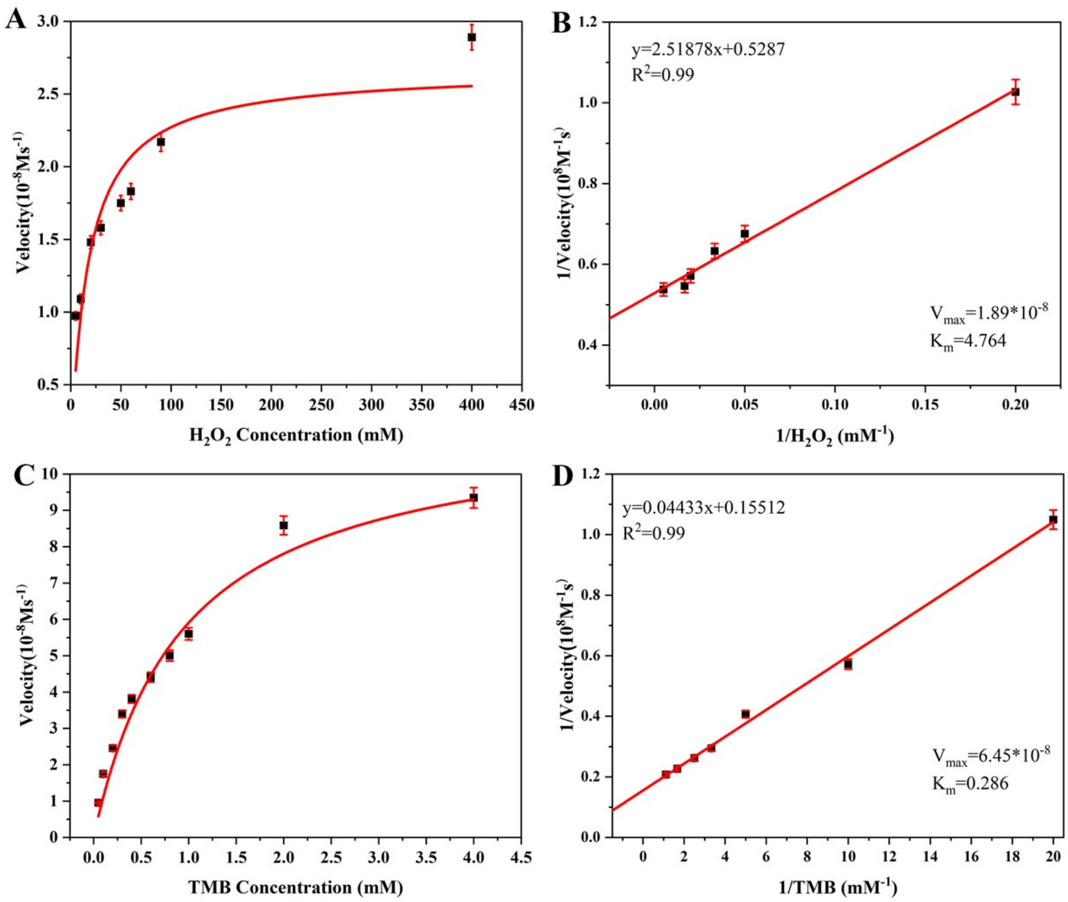

Fig. S7. (A)Reaction rate curve, (B)double reciprocal curve of reaction rate and substrate concentration of Fe-based nanozyme, using H_2O_2 as a substrate. (C)Reaction rate curve, (D)double reciprocal curve of reaction rate and substrate concentration of Fe-based nanozyme. Using TMB as a substrate.

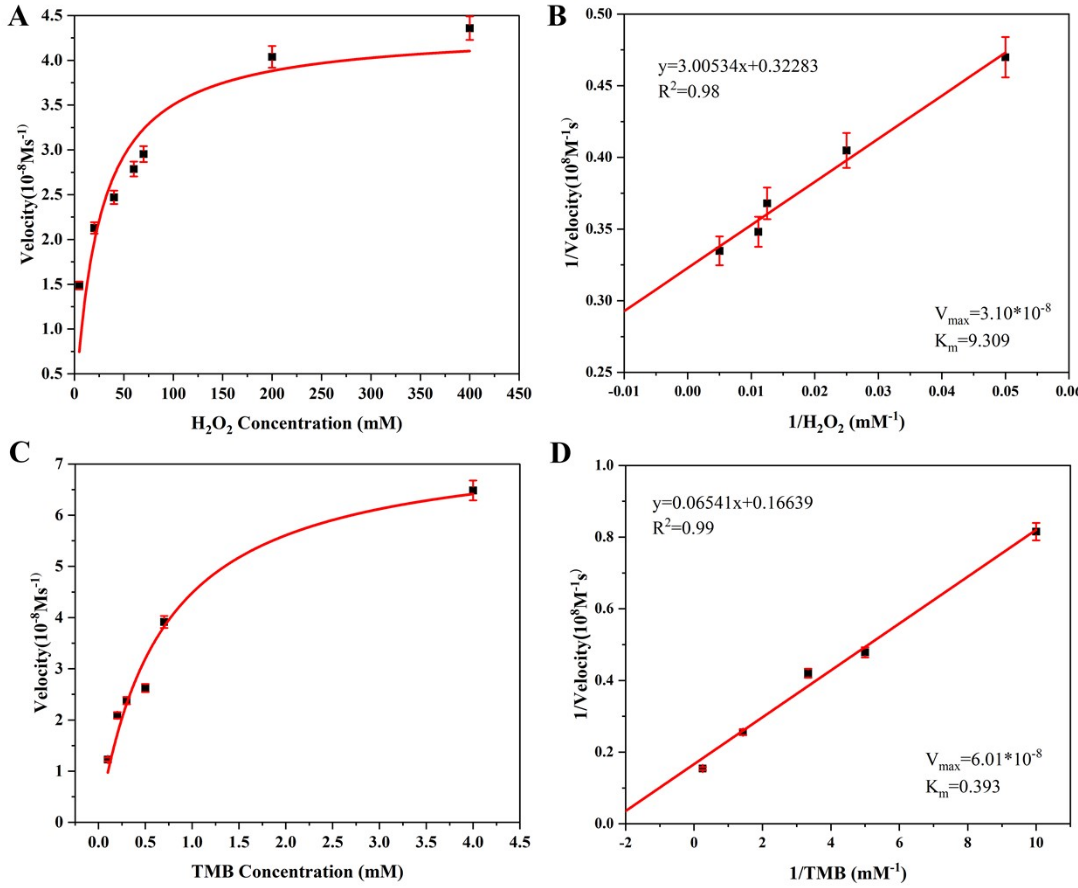

Fig. S8. (A)Reaction rate curve, (B)double reciprocal curve of reaction rate and substrate concentration of Zn-based nanozyme, using H_2O_2 as a substrate. (C)Reaction rate curve, (D)double reciprocal curve of reaction rate and substrate concentration of Zn-based nanozyme. Using TMB as a substrate.

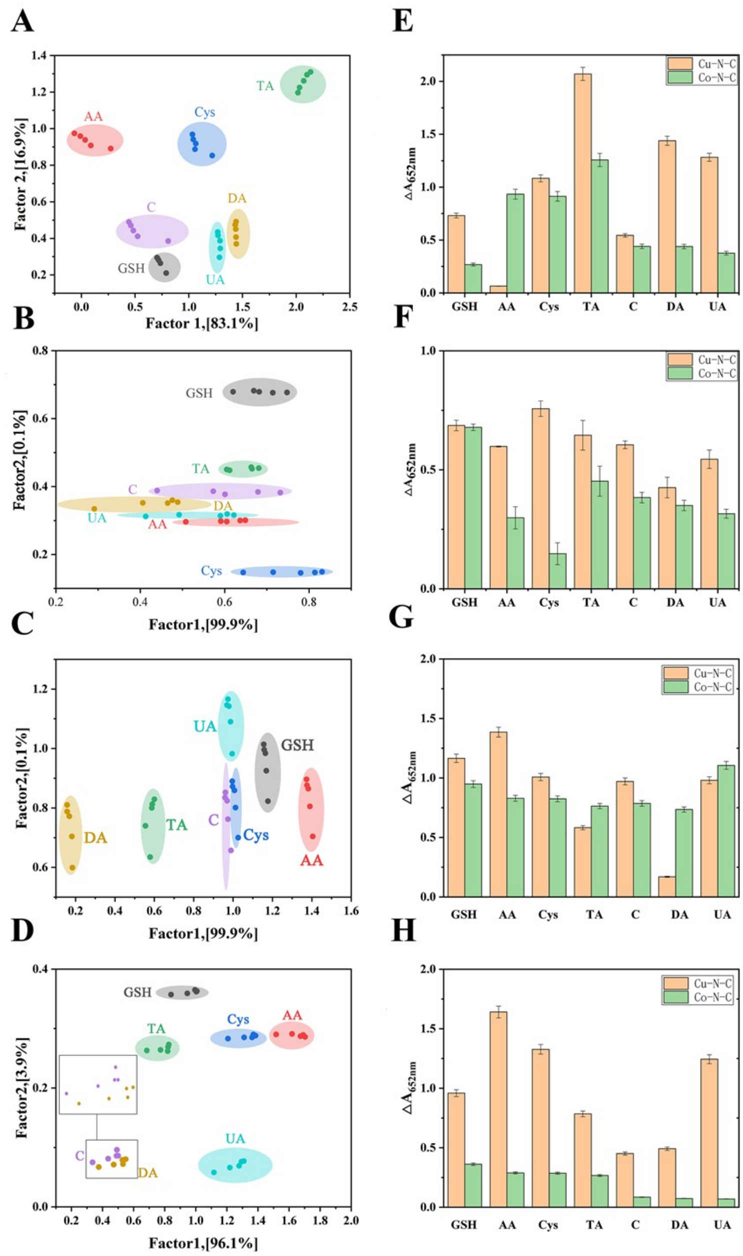

Fig. S9. (A-D)LDA Canonical score plot, (E-H) Fingerprints.(A, E)50μM，（B, F）1μM，（C, G）100nM，（D, H）10nM. Cu-based nanozyme, Co-based nanozyme sensor array.

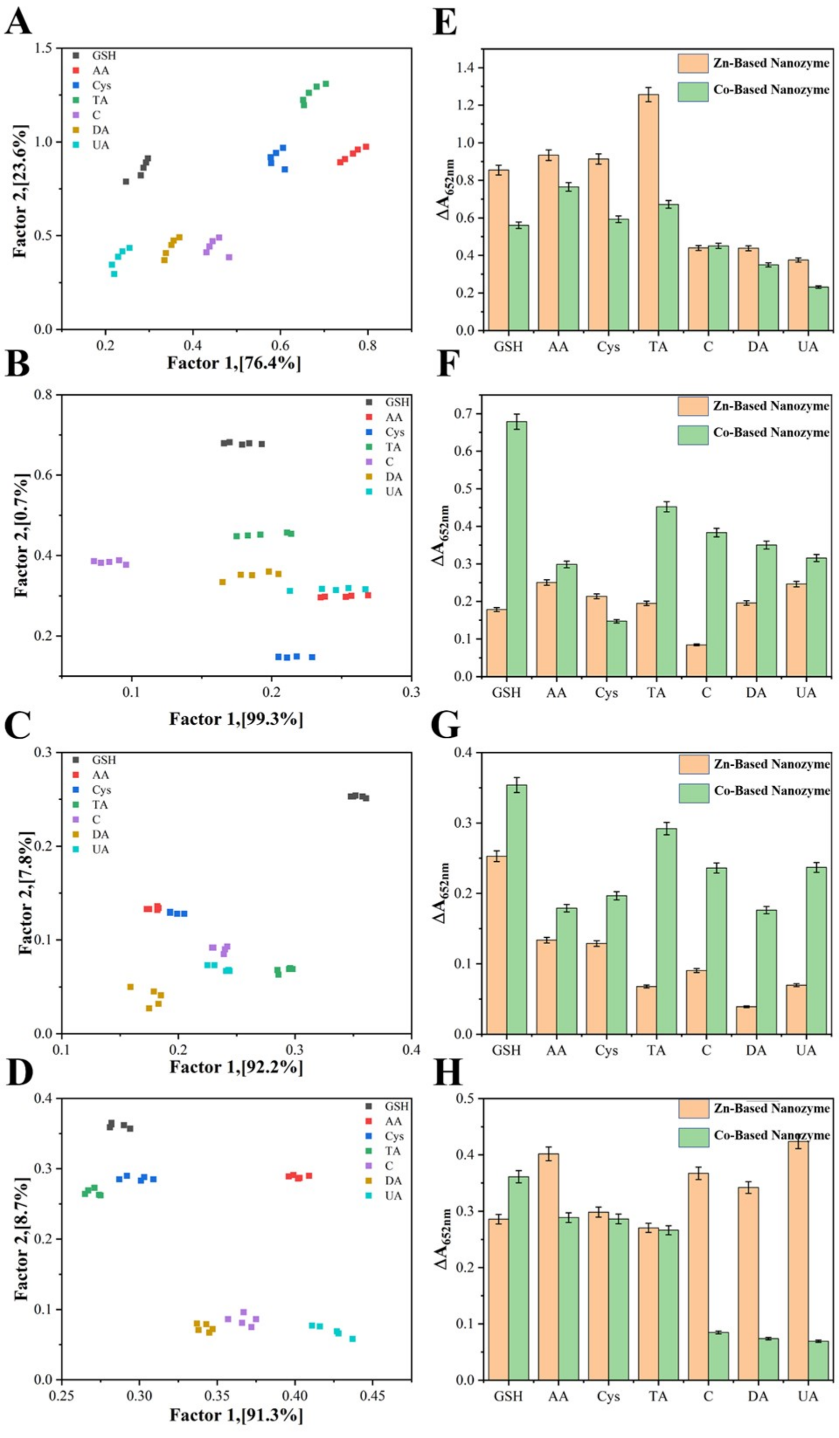

Fig. S10. (A-D)LDA Canonical score plot, (E-H) Fingerprints.(A, E)50μM，（B, F）1μM，（C, G）100nM，（D, H）10nM. Zn-based nanozyme, Co-based nanozyme sensor array.

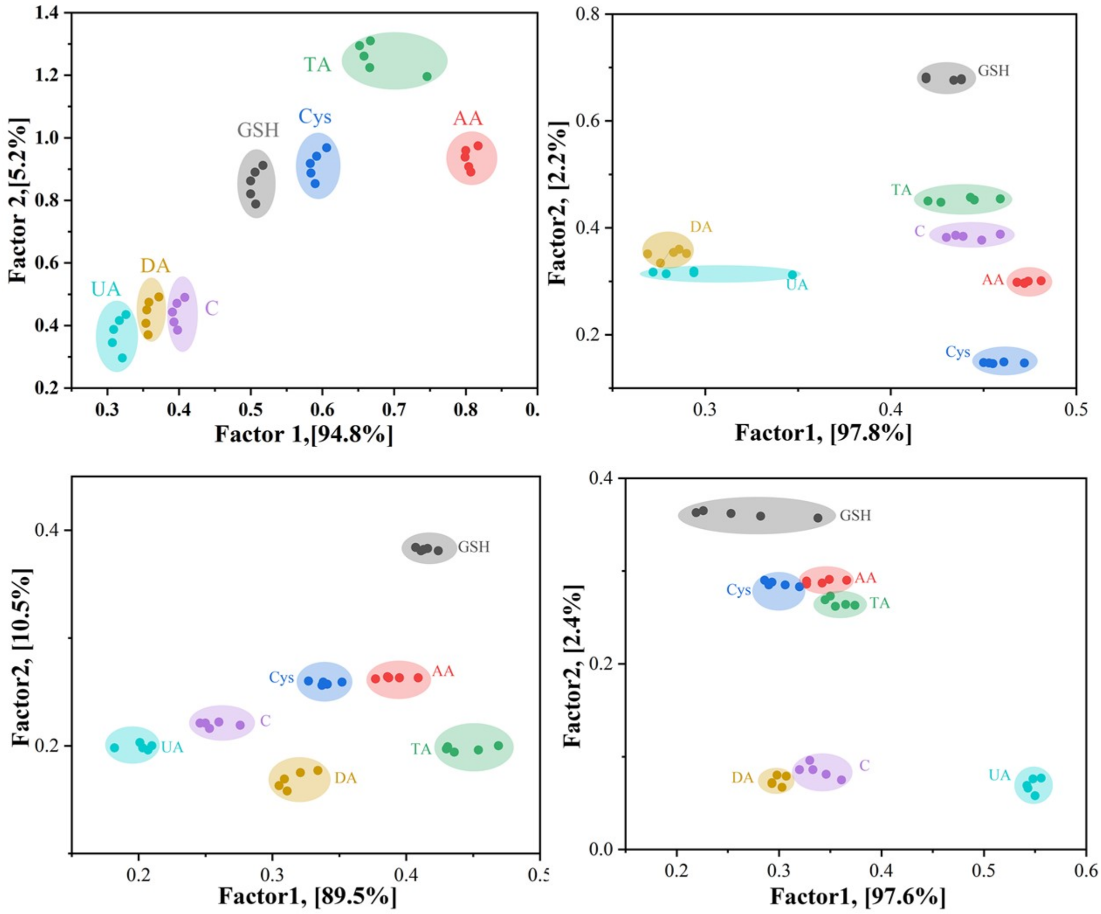

Fig. S11. LDA Canonical score plots for 50 μM, 1 μM, 100 nM, 10 nM antioxidants. Fe-based nanozyme, Co-based nanozyme sensor array.

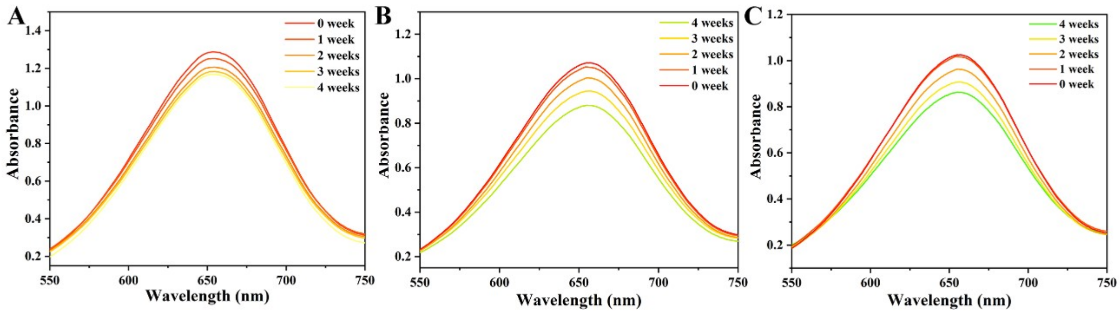

Fig. S12. Nanozyme activity with different storage times, (A)Fe-based nanozyme, (B)Cu-based nanozyme, (C) Zn-based nanozyme.

Table S0. Comparison of steady-state kinetic parameters (Km and V_{max}) between Metal-based nanozymes and other materials.

Materials	TMB		H_2O_2		Reference
	V_{max}(10^{-8}M·S^{-1})	Km(mM)	V_{max}(10^{-8}M·S^{-1})	Km(mM)	
Co-based nanozyme	**3.83**	**0.160**	**1.08**	**2.64**	**This work**
Fe-based nanozyme	**6.45**	**0.286**	**1.89**	**4.76**	**This work**
Cu-based nanozyme	**11.5**	**0.299**	**4.92**	**3.59**	**This work**
Zn-based nanozyme	**6.01**	**0.393**	**3.10**	**9.31**	**This work**
CuNCs	**7.20**	**1.125**	**16.80**	**2.52**	**[1]**
Fe_3O_4 NPs	**3.44**	**0.095**	**9.78**	**154**	**[2]**
HRP	**10**	**0.43**	**8.71**	**3.7**	**[3]**
N-GODs	**0.38**	**0.112**	**0.14**	**0.101**	**[4]**

Table S1 The data of the colorimetric response patterns against AA at different concentrations using Cu-based nanozyme.

AA concentration	A_0-A Cu-based nanozyme
1μM	0.713
900nM	0.666
800nM	0.625
500nM	0.582
400nM	0.544
200nM	0.458
100nM	0.445
50nM	0.434
10nM	0.417

Table S2 The data of the colorimetric response patterns against Cys at different concentrations using Cu-based nanozyme.

Cys concentration	A_0-A Cu-based nanozyme
700nM	1.004
600nM	0.993
500nM	0.979
400nM	0.973
300nM	0.954
200nM	0.939
100nM	0.932
50nM	0.923
10nM	0.909

Table S3 The data of the colorimetric response patterns against AA at different concentrations using Fe-based nanozyme.

AA concentration	A_0-A Fe-based nanozyme
1μM	0.3628
600nM	0.2298
500nM	0.2204
400nM	0.208
10nM	0.0778

Table S4 The data of the colorimetric response patterns against GSH at different concentrations using Fe-based nanozyme.

GSH concentration	A_0-A Fe-based nanozyme
1μM	0.3932
800nM	0.3622
700nM	0.3414
600nM	0.3282
400nM	0.2644
300nM	0.2506
200nM	0.2442
100nM	0.2252
50nM	0.2008
10nM	0.1856

Table S5 data of the colorimetric response patterns against AA at different concentrations using Zn-based nanozyme.

AA concentration	A_0-A Zn-based nanozyme
700nM	0.3948
500nM	0.2742
300nM	0.2516
100nM	0.1408
10nM	0.1174

Table S6 The data of the colorimetric response patterns against GSH at different concentrations using Zn-based nanozyme.

GSH concentration	A_0-A Zn-based nanozyme
900nM	0.2814
700nM	0.2278
500nM	0.1612
300nM	0.1014
100nM	0.0684
10nM	0.0114

Table S7 The training matrix of the colorimetric response patterns against 7 antioxidants using Fe-based nanozyme, Co-based nanozyme sensor assay at the concentration of 50μM.

Antioxidants	A_0-A Fe-based nanozyme	A_0-A Co-based nanozyme
GSH	0.507	0.788
GSH	0.5	0.821
GSH	0.5	0.862
GSH	0.506	0.89
GSH	0.517	0.912
AA	0.807	0.891
AA	0.804	0.908
AA	0.799	0.938
AA	0.8	0.959
AA	0.817	0.974
Cys	0.59	0.853
Cys	0.584	0.887
Cys	0.583	0.918
Cys	0.592	0.941
Cys	0.606	0.968
TA	0.746	1.196
TA	0.666	1.224
TA	0.658	1.261
TA	0.652	1.294
TA	0.667	1.31
C	0.398	0.385
C	0.393	0.411
C	0.391	0.443
C	0.397	0.471
C	0.408	0.49
DA	0.357	0.37
DA	0.354	0.407
DA	0.355	0.45
DA	0.358	0.474
DA	0.372	0.491
UA	0.321	0.296
UA	0.307	0.345
UA	0.309	0.387
UA	0.317	0.416
UA	0.326	0.435

Table S8 The training matrix of the colorimetric response patterns against 7 antioxidants using Fe-based nanozyme, Co-based nanozyme sensor assay at the concentration of 1μM.

Antioxidants	A_0-A Fe-based nanozyme	A_0-A Co-based nanozyme
GSH	0.419	0.679
GSH	0.419	0.682
GSH	0.434	0.676
GSH	0.438	0.679
GSH	0.438	0.677
AA	0.472	0.296
AA	0.468	0.298
AA	0.472	0.297
AA	0.474	0.3
AA	0.481	0.301
Cys	0.453	0.147
Cys	0.45	0.148
Cys	0.455	0.146
Cys	0.461	0.149
Cys	0.472	0.147
TA	0.427	0.448
TA	0.42	0.45
TA	0.445	0.452
TA	0.443	0.457
TA	0.459	0.454
C	0.459	0.388
C	0.435	0.386
C	0.43	0.382
C	0.439	0.384
C	0.449	0.377
DA	0.276	0.334
DA	0.29	0.352
DA	0.269	0.351
DA	0.286	0.36
DA	0.283	0.354
UA	0.347	0.312
UA	0.272	0.317
UA	0.279	0.314
UA	0.294	0.319
UA	0.294	0.316

Table S9 The training matrix of the colorimetric response patterns against 7 antioxidants using Fe-based nanozyme, Co-based nanozyme sensor assay at the concentration of 100nM.

Antioxidants	A_0-A Fe-based nanozyme	A_0-A Co-based nanozyme
GSH	0.413	0.382
GSH	0.407	0.384
GSH	0.411	0.381
GSH	0.416	0.383
GSH	0.424	0.381
AA	0.387	0.263
AA	0.386	0.264
AA	0.377	0.262
AA	0.395	0.263
AA	0.409	0.263
Cys	0.338	0.259
Cys	0.327	0.26
Cys	0.337	0.256
Cys	0.352	0.259
Cys	0.341	0.257
TA	0.436	0.194
TA	0.431	0.199
TA	0.43	0.197
TA	0.469	0.2
TA	0.454	0.196
C	0.253	0.216
C	0.246	0.221
C	0.25	0.221
C	0.26	0.222
C	0.276	0.219
DA	0.311	0.158
DA	0.305	0.163
DA	0.309	0.169
DA	0.321	0.175
DA	0.334	0.177
UA	0.203	0.198
UA	0.182	0.198
UA	0.207	0.196
UA	0.201	0.203
UA	0.21	0.2

Table S10 The training matrix of the colorimetric response patterns against 7 antioxidants using Fe-based nanozyme, Co-based nanozyme sensor assay at the concentration of 10nM.

Antioxidants	A_0-A Fe-based nanozyme	A_0-A Co-based nanozyme
GSH	0.338	0.357
GSH	0.282	0.359
GSH	0.253	0.362
GSH	0.226	0.365
GSH	0.219	0.363
AA	0.366	0.29
AA	0.349	0.291
AA	0.342	0.287
AA	0.327	0.289
AA	0.327	0.286
Cys	0.32	0.283
Cys	0.306	0.285
Cys	0.29	0.285
Cys	0.286	0.29
Cys	0.293	0.288
TA	0.374	0.263
TA	0.365	0.264
TA	0.355	0.262
TA	0.345	0.269
TA	0.35	0.273
C	0.361	0.075
C	0.346	0.081
C	0.333	0.086
C	0.33	0.096
C	0.32	0.086
DA	0.303	0.067
DA	0.293	0.071
DA	0.293	0.072
DA	0.298	0.08
DA	0.307	0.079
UA	0.55	0.058
UA	0.543	0.066
UA	0.542	0.069
UA	0.548	0.076
UA	0.556	0.077

Table S11 The training matrix of the colorimetric response patterns against 7 antioxidants using Cu-based nanozyme, Co-based nanozyme sensor assay at the concentration of 50μM.

Antioxidants	A_0-A Cu-based nanozyme	A_0-A Co-based nanozyme
GSH	0.841	0.357
GSH	0.946	0.359
GSH	1.004	0.362
GSH	0.995	0.365
GSH	1.007	0.363
AA	1.517	0.29
AA	1.619	0.291
AA	1.674	0.287
AA	1.691	0.289
AA	1.703	0.286
Cys	1.207	0.283
Cys	1.311	0.285
Cys	1.362	0.285
Cys	1.371	0.29
Cys	1.385	0.288
TA	0.685	0.263
TA	0.773	0.264
TA	0.819	0.262
TA	0.822	0.269
TA	0.826	0.273
C	0.336	0.075
C	0.437	0.081
C	0.49	0.086
C	0.493	0.096
C	0.501	0.086
DA	0.376	0.067
DA	0.472	0.071
DA	0.532	0.072
DA	0.549	0.08
DA	0.528	0.079
UA	1.117	0.058
UA	1.219	0.066
UA	1.279	0.069
UA	1.294	0.076
UA	1.309	0.077

Table S12 The training matrix of the colorimetric response patterns against 7 antioxidants using Cu-based nanozyme, Co-based nanozyme sensor assay at the concentration of 1μM.

Antioxidants	A_0-A Cu-based nanozyme	A_0-A Co-based nanozyme
GSH	0.62	0.679
GSH	0.669	0.682
GSH	0.714	0.676
GSH	0.682	0.679
GSH	0.748	0.677
AA	0.508	0.296
AA	0.591	0.298
AA	0.605	0.297
AA	0.637	0.3
AA	0.649	0.301
Cys	0.644	0.147
Cys	0.715	0.148
Cys	0.78	0.146
Cys	0.831	0.149
Cys	0.814	0.147
TA	0.612	0.448
TA	0.605	0.45
TA	0.665	0.452
TA	0.663	0.457
TA	0.681	0.454
C	0.44	0.388
C	0.573	0.386
C	0.732	0.382
C	0.679	0.384
C	0.601	0.377
DA	0.291	0.334
DA	0.406	0.352
DA	0.465	0.351
DA	0.476	0.36
DA	0.489	0.354
UA	0.413	0.312
UA	0.492	0.317
UA	0.59	0.314
UA	0.606	0.319
UA	0.622	0.316

Table S13 The training matrix of the colorimetric response patterns against 7 antioxidants using Cu-based nanozyme, Co-based nanozyme sensor assay at the concentration of 100nM.

Antioxidants	A_0-A Cu-based nanozyme	A_0-A Co-based nanozyme
GSH	1.177	0.823
GSH	1.169	0.925
GSH	1.164	0.984
GSH	1.158	0.996
GSH	1.156	1.014
AA	1.405	0.704
AA	1.39	0.805
AA	1.382	0.865
AA	1.375	0.876
AA	1.373	0.896
Cys	1.026	0.7
Cys	1.012	0.801
Cys	1.007	0.859
Cys	0.997	0.872
Cys	0.996	0.89
TA	0.579	0.635
TA	0.555	0.74
TA	0.587	0.8
TA	0.59	0.813
TA	0.6	0.829
C	0.989	0.657
C	0.974	0.762
C	0.97	0.824
C	0.959	0.835
C	0.961	0.852
DA	0.184	0.599
DA	0.181	0.704
DA	0.168	0.772
DA	0.157	0.788
DA	0.157	0.81
UA	0.995	0.982
UA	0.987	1.09
UA	0.979	1.142
UA	0.969	1.146
UA	0.974	1.166

Table S14 The training matrix of the colorimetric response patterns against 7 antioxidants using Cu-based nanozyme, Co-based nanozyme sensor assay at the concentration of 10nM.

Antioxidants	A_0-A Cu-based nanozyme	A_0-A Co-based nanozyme
GSH	0.841	0.357
GSH	0.946	0.359
GSH	1.004	0.362
GSH	0.995	0.365
GSH	1.007	0.363
AA	1.517	0.29
AA	1.619	0.291
AA	1.674	0.287
AA	1.691	0.289
AA	1.703	0.286
Cys	1.207	0.283
Cys	1.311	0.285
Cys	1.362	0.285
Cys	1.371	0.29
Cys	1.385	0.288
TA	0.685	0.263
TA	0.773	0.264
TA	0.819	0.262
TA	0.822	0.269
TA	0.826	0.273
C	0.336	0.075
C	0.437	0.081
C	0.49	0.086
C	0.493	0.096
C	0.501	0.086
DA	0.376	0.067
DA	0.472	0.071
DA	0.532	0.072
DA	0.549	0.08
DA	0.528	0.079
UA	1.117	0.058
UA	1.219	0.066
UA	1.279	0.069
UA	1.294	0.076
UA	1.309	0.077

Table S15 The training matrix of the colorimetric response patterns against 7 antioxidants using Zn-based nanozyme, Co-based nanozyme sensor assay at the concentration of 50μM.

Antioxidants	A_0-A Cu-based nanozyme	A_0-A Co-based nanozyme
GSH	0.564	0.788
GSH	0.544	0.821
GSH	0.556	0.862
GSH	0.563	0.89
GSH	0.577	0.912
AA	0.737	0.891
AA	0.748	0.908
AA	0.766	0.938
AA	0.777	0.959
AA	0.796	0.974
Cys	0.61	0.853
Cys	0.579	0.887
Cys	0.578	0.918
Cys	0.59	0.941
Cys	0.606	0.968
TA	0.654	1.196
TA	0.652	1.224
TA	0.665	1.261
TA	0.683	1.294
TA	0.704	1.31
C	0.483	0.385
C	0.431	0.411
C	0.438	0.443
C	0.445	0.471
C	0.46	0.49
DA	0.335	0.37
DA	0.338	0.407
DA	0.351	0.45
DA	0.356	0.474
DA	0.369	0.491
UA	0.22	0.296
UA	0.215	0.345
UA	0.229	0.387
UA	0.239	0.416
UA	0.255	0.435

Table S16 The training matrix of the colorimetric response patterns against 7 antioxidants using Zn-based nanozyme, Co-based nanozyme sensor assay at the concentration of 1μM.

Antioxidants	A_0-A Cu-based nanozyme	A_0-A Co-based nanozyme
GSH	0.166	0.679
GSH	0.17	0.682
GSH	0.179	0.676
GSH	0.184	0.679
GSH	0.193	0.677
AA	0.235	0.296
AA	0.238	0.298
AA	0.253	0.297
AA	0.257	0.3
AA	0.269	0.301
Cys	0.205	0.147
Cys	0.205	0.148
Cys	0.211	0.146
Cys	0.218	0.149
Cys	0.229	0.147
TA	0.175	0.448
TA	0.183	0.45
TA	0.192	0.452
TA	0.211	0.457
TA	0.214	0.454
C	0.091	0.388
C	0.073	0.386
C	0.078	0.382
C	0.084	0.384
C	0.096	0.377
DA	0.165	0.334
DA	0.178	0.352
DA	0.186	0.351
DA	0.198	0.36
DA	0.205	0.354
UA	0.213	0.312
UA	0.236	0.317
UA	0.246	0.314
UA	0.255	0.319
UA	0.267	0.316

Table S17 The training matrix of the colorimetric response patterns against 7 antioxidants using Zn-based nanozyme, Co-based nanozyme sensor assay at the concentration of 100nM.

Antioxidants	A_0-A Cu-based nanozyme	A_0-A Co-based nanozyme
GSH	0.361	0.251
GSH	0.348	0.253
GSH	0.358	0.253
GSH	0.35	0.253
GSH	0.352	0.254
AA	0.182	0.132
AA	0.175	0.133
AA	0.183	0.134
AA	0.173	0.133
AA	0.182	0.136
Cys	0.199	0.128
Cys	0.193	0.129
Cys	0.205	0.128
Cys	0.193	0.129
Cys	0.193	0.13
TA	0.286	0.063
TA	0.285	0.068
TA	0.298	0.069
TA	0.296	0.07
TA	0.295	0.069
C	0.239	0.085
C	0.24	0.09
C	0.242	0.093
C	0.229	0.092
C	0.23	0.092
DA	0.175	0.027
DA	0.183	0.032
DA	0.185	0.041
DA	0.179	0.045
DA	0.159	0.05
UA	0.244	0.067
UA	0.241	0.067
UA	0.243	0.068
UA	0.231	0.073
UA	0.225	0.073

Table S18 The training matrix of the colorimetric response patterns against 7 antioxidants using Zn-based nanozyme, Co-based nanozyme sensor assay at the concentration of 10nM.

Antioxidants	A_0-A Cu-based nanozyme	A_0-A Co-based nanozyme
GSH	0.148	0.357
GSH	0.115	0.359
GSH	0.043	0.362
GSH	0.021	0.365
GSH	0.029	0.363
AA	0.219	0.29
AA	0.184	0.291
AA	0.159	0.287
AA	0.16	0.289
AA	0.147	0.286
Cys	0.351	0.283
Cys	0.236	0.285
Cys	0.233	0.285
Cys	0.221	0.29
Cys	0.218	0.288
TA	0.337	0.263
TA	0.188	0.264
TA	0.164	0.262
TA	0.163	0.269
TA	0.155	0.273
C	0.239	0.075
C	0.111	0.081
C	0.098	0.086
C	0.087	0.096
C	0.088	0.086
DA	0.165	0.067
DA	0.099	0.071
DA	0.095	0.072
DA	0.088	0.08
DA	0.085	0.079
UA	0.298	0.058
UA	0.155	0.066
UA	0.149	0.069
UA	0.144	0.076
UA	0.141	0.077

Table S19 The training matrix of the colorimetric response patterns against TA, UA binary mixture and TA, GSH, DA ternary mixture at 10 nM using Cu-based nanozyme, Co-based nanozyme assay.

proportion of mixture	A_0-A Cu-based nanozyme	A_0-A Co-based nanozyme
TA:UA=9:1	1.427	1.158
TA:UA=9:1	1.527	1.156
TA:UA=9:1	1.586	1.153
TA:UA=9:1	1.592	1.156
TA:UA=9:1	1.609	1.152
TA:UA=6:4	1.038	0.855
TA:UA=6:4	1.137	0.851
TA:UA=6:4	1.199	0.847
TA:UA=6:4	1.191	0.849
TA:UA=6:4	1.216	0.845
TA:UA=5:5	1.263	0.806
TA:UA=5:5	1.372	0.801
TA:UA=5:5	1.436	0.796
TA:UA=5:5	1.45	0.804
TA:UA=5:5	1.469	0.798
TA:UA=4:6	1.333	1.35
TA:UA=4:6	1.426	1.352
TA:UA=4:6	1.514	1.339
TA:UA=4:6	1.515	1.339
TA:UA=4:6	1.53	1.335
TA:UA=1:9	1.286	0.772
TA:UA=1:9	1.403	0.769
TA:UA=1:9	1.452	0.767
TA:UA=1:9	1.468	0.776
TA:UA=1:9	1.483	0.769
TA:GSH:DA=1:1:1	0.88	0.845
TA:GSH:DA=1:1:1	0.856	0.841
TA:GSH:DA=1:1:1	0.851	0.849
TA:GSH:DA=1:1:1	0.847	0.845
TA:GSH:DA=1:1:1	0.847	0.839
TA:GSH:DA=1:2:1	0.868	0.883
TA:GSH:DA=1:2:1	0.85	0.885
TA:GSH:DA=1:2:1	0.873	0.873
TA:GSH:DA=1:2:1	0.86	0.873
TA:GSH:DA=1:2:1	0.865	0.867
TA:GSH:DA=1:2:3	0.973	0.808
TA:GSH:DA=1:2:3	0.943	0.803
TA:GSH:DA=1:2:3	0.955	0.806
TA:GSH:DA=1:2:3	0.949	0.805

TA:GSH:DA=1:2:3	0.949	0.799
TA:GSH:DA=2:1:1	0.674	0.89
TA:GSH:DA=2:1:1	0.66	0.888
TA:GSH:DA=2:1:1	0.658	0.884
TA:GSH:DA=2:1:1	0.666	0.887
TA:GSH:DA=2:1:1	0.667	0.885
TA:GSH:DA=2:2:1	1.012	0.881
TA:GSH:DA=2:2:1	0.995	0.885
TA:GSH:DA=2:2:1	0.993	0.88
TA:GSH:DA=2:2:1	0.989	0.877
TA:GSH:DA=2:2:1	0.988	0.873
TA:GSH:DA=2:3:1	0.743	0.749
TA:GSH:DA=2:3:1	0.739	0.752
TA:GSH:DA=2:3:1	0.741	0.749
TA:GSH:DA=2:3:1	0.74	0.753
TA:GSH:DA=2:3:1	0.74	0.748
TA:GSH:DA=3:1:2	0.701	0.914
TA:GSH:DA=3:1:2	0.688	0.915
TA:GSH:DA=3:1:2	0.685	0.913
TA:GSH:DA=3:1:2	0.684	0.915
TA:GSH:DA=3:1:2	0.687	0.915
TA:GSH:DA=3:2:1	0.919	0.846
TA:GSH:DA=3:2:1	0.91	0.852
TA:GSH:DA=3:2:1	0.919	0.849
TA:GSH:DA=3:2:1	0.917	0.848
TA:GSH:DA=3:2:1	0.919	0.844
TA:GSH:DA=3:1:1	0.688	0.518
TA:GSH:DA=3:1:1	0.667	0.528
TA:GSH:DA=3:1:1	0.667	0.525
TA:GSH:DA=3:1:1	0.664	0.521
TA:GSH:DA=3:1:1	0.667	0.516

Table S20 The training matrix of the colorimetric response patterns against AA, DA binary mixture and AA, Cys, UA ternary mixture at 10 nM using Fe-based nanozyme, Co-based nanozyme assay.

proportion of mixture	A_0-A Fe-based nanozyme	A_0-A Co-based nanozyme
AA:DA=2:8	0.454	1.135
AA:DA=2:8	0.444	1.129
AA:DA=2:8	0.44	1.131
AA:DA=2:8	0.437	1.134
AA:DA=2:8	0.451	1.125
AA:DA=4:6	0.48	0.981
AA:DA=4:6	0.475	0.982
AA:DA=4:6	0.467	0.98
AA:DA=4:6	0.468	0.982
AA:DA=4:6	0.478	0.978
AA:DA=5:5	0.425	1.061
AA:DA=5:5	0.416	1.041
AA:DA=5:5	0.418	1.056
AA:DA=5:5	0.423	1.046
AA:DA=5:5	0.435	1.044
AA:DA=6:4	0.456	1.009
AA:DA=6:4	0.444	1.019
AA:DA=6:4	0.448	1.02
AA:DA=6:4	0.454	1.021
AA:DA=6:4	0.466	1.02
AA:DA=8:2	0.497	0.979
AA:DA=8:2	0.496	0.981
AA:DA=8:2	0.5	0.979
AA:DA=8:2	0.499	0.98
AA:DA=8:2	0.515	0.978
AA:Cys:UA=1:2:3	0.485	1.153
AA:Cys:UA=1:2:3	0.473	1.154
AA:Cys:UA=1:2:3	0.477	1.148
AA:Cys:UA=1:2:3	0.481	1.151
AA:Cys:UA=1:2:3	0.491	1.147
AA:Cys:UA=2:1:1	0.432	0.717
AA:Cys:UA=2:1:1	0.425	0.722
AA:Cys:UA=2:1:1	0.429	0.723
AA:Cys:UA=2:1:1	0.434	0.726
AA:Cys:UA=2:1:1	0.445	0.724
AA:Cys:UA=2:2:1	0.449	0.951
AA:Cys:UA=2:2:1	0.442	0.951
AA:Cys:UA=2:2:1	0.442	0.951
AA:Cys:UA=2:2:1	0.447	0.954

AA:Cys:UA=2:2:1	0.456	0.949
AA:Cys:UA=2:3:1	0.486	0.897
AA:Cys:UA=2:3:1	0.48	0.894
AA:Cys:UA=2:3:1	0.475	0.889
AA:Cys:UA=2:3:1	0.475	0.891
AA:Cys:UA=2:3:1	0.486	0.885
AA:Cys:UA=3:1:2	0.464	0.849
AA:Cys:UA=3:1:2	0.457	0.867
AA:Cys:UA=3:1:2	0.457	0.864
AA:Cys:UA=3:1:2	0.462	0.86
AA:Cys:UA=3:1:2	0.474	0.854
AA:Cys:UA=3:2:1	0.488	0.613
AA:Cys:UA=3:2:1	0.483	0.609
AA:Cys:UA=3:2:1	0.479	0.609
AA:Cys:UA=3:2:1	0.482	0.613
AA:Cys:UA=3:2:1	0.494	0.607
AA:Cys:UA=3:1:1	0.554	0.633
AA:Cys:UA=3:1:1	0.544	0.637
AA:Cys:UA=3:1:1	0.546	0.632
AA:Cys:UA=3:1:1	0.548	0.633
AA:Cys:UA=3:1:1	0.554	0.63

Table S21 The training matrix of the colorimetric response patterns against GSH, Cys binary mixture and GSH, AA, TA ternary mixture at 10 nM using Zn-based nanozyme, Co-based nanozyme assay.

proportion of mixture	A_0-A Zn-based nanozyme	A_0-A Co-based nanozyme
GSH:Cys=9:1	0.213	0.586
GSH:Cys=9:1	0.205	0.57
GSH:Cys=9:1	0.223	0.577
GSH:Cys=9:1	0.22	0.576
GSH:Cys=9:1	0.217	0.569
GSH:Cys=8:2	0.259	1.254
GSH:Cys=8:2	0.256	1.242
GSH:Cys=8:2	0.278	1.248
GSH:Cys=8:2	0.276	1.25
GSH:Cys=8:2	0.277	1.25
GSH:Cys=7:3	0.34	0.19
GSH:Cys=7:3	0.334	0.201
GSH:Cys=7:3	0.351	0.186
GSH:Cys=7:3	0.35	0.194
GSH:Cys=7:3	0.345	0.193
GSH:Cys=6:4	0.4	0.402
GSH:Cys=6:4	0.392	0.392
GSH:Cys=6:4	0.404	0.391
GSH:Cys=6:4	0.408	0.387
GSH:Cys=6:4	0.411	0.394
GSH:Cys=5:5	0.409	0.549
GSH:Cys=5:5	0.4	0.542
GSH:Cys=5:5	0.414	0.544
GSH:Cys=5:5	0.416	0.536
GSH:Cys=5:5	0.416	0.53
GSH:Cys=4:6	0.253	0.498
GSH:Cys=4:6	0.246	0.487
GSH:Cys=4:6	0.262	0.475
GSH:Cys=4:6	0.264	0.487
GSH:Cys=4:6	0.266	0.48
GSH:Cys=3:7	0.316	0.602
GSH:Cys=3:7	0.309	0.587
GSH:Cys=3:7	0.314	0.596
GSH:Cys=3:7	0.312	0.579
GSH:Cys=3:7	0.328	0.576
GSH:Cys=2:8	0.527	0.245
GSH:Cys=2:8	0.517	0.253
GSH:Cys=2:8	0.534	0.249
GSH:Cys=2:8	0.532	0.252

GSH:Cys=2:8	0.531	0.256
GSH:Cys=1:9	0.543	0.486
GSH:Cys=1:9	0.531	0.479
GSH:Cys=1:9	0.551	0.479
GSH:Cys=1:9	0.545	0.482
GSH:Cys=1:9	0.548	0.48
GSH:AA:TA=1:1:1	0.224	0.247
GSH:AA:TA=1:1:1	0.212	0.24
GSH:AA:TA=1:1:1	0.223	0.245
GSH:AA:TA=1:1:1	0.22	0.251
GSH:AA:TA=1:1:1	0.22	0.166
GSH:AA:TA=2:1:1	0.272	0.155
GSH:AA:TA=2:1:1	0.278	0.162
GSH:AA:TA=2:1:1	0.29	0.164
GSH:AA:TA=2:1:1	0.289	0.169
GSH:AA:TA=2:1:1	0.289	0.166
GSH:AA:TA=1:2:1	0.302	0.116
GSH:AA:TA=1:2:1	0.296	0.113
GSH:AA:TA=1:2:1	0.313	0.119
GSH:AA:TA=1:2:1	0.309	0.122
GSH:AA:TA=1:2:1	0.31	0.128
GSH:AA:TA=3:2:1	0.399	0.085
GSH:AA:TA=3:2:1	0.398	0.084
GSH:AA:TA=3:2:1	0.416	0.085
GSH:AA:TA=3:2:1	0.413	0.092
GSH:AA:TA=3:2:1	0.412	0.097
GSH:AA:TA=1:2:3	0.343	0.046
GSH:AA:TA=1:2:3	0.334	0.044
GSH:AA:TA=1:2:3	0.35	0.053
GSH:AA:TA=1:2:3	0.339	0.073
GSH:AA:TA=1:2:3	0.351	0.052

Table S22 The training matrix of the colorimetric response patterns against the the antioxidants at 10 nM and other interfering species at 1μM using Cu-based nanozyme, Co-based nanozyme sensor assay.

Antioxidants and interfering species	A_0-A Cu-based nanozyme	A_0-A Co-based nanozyme
GSH	0.841	0.357
GSH	0.946	0.359
GSH	1.004	0.362
GSH	0.995	0.365
GSH	1.007	0.363
AA	1.517	0.29
AA	1.619	0.291
AA	1.674	0.287
AA	1.691	0.289
AA	1.703	0.286
Cys	1.207	0.283
Cys	1.311	0.285
Cys	1.362	0.285
Cys	1.371	0.29
Cys	1.385	0.288
TA	0.685	0.263
TA	0.773	0.264
TA	0.819	0.262
TA	0.822	0.269
TA	0.826	0.273
C	0.336	0.075
C	0.437	0.081
C	0.49	0.086
C	0.493	0.096
C	0.501	0.086
DA	0.376	0.067
DA	0.472	0.071
DA	0.532	0.072
DA	0.549	0.08
DA	0.528	0.079
UA	1.117	0.058
UA	1.219	0.066
UA	1.279	0.069
UA	1.294	0.076
UA	1.309	0.077
CA	0.932	0.478
CA	1.029	0.505
CA	1.098	0.546

CA	1.109	0.573
CA	1.118	0.594
GA	0.874	0.347
GA	0.976	0.376
GA	1.047	0.41
GA	1.065	0.436
GA	1.076	0.456
TAA	0.834	0.776
TAA	0.943	0.807
TAA	1.001	0.845
TAA	1.013	0.869
TAA	1.032	0.888

Table S23 The training matrix of the colorimetric response patterns against the the antioxidants at 10 nM and other interfering species at 1μM using Fe-based nanozyme, Co-based nanozyme sensor assay.

Antioxidants and interfering species	A_0-A Fe-based nanozyme	A_0-A Co-based nanozyme
GSH	0.338	0.357
GSH	0.282	0.359
GSH	0.253	0.362
GSH	0.226	0.365
GSH	0.219	0.363
AA	0.366	0.29
AA	0.349	0.291
AA	0.342	0.287
AA	0.327	0.289
AA	0.327	0.286
Cys	0.32	0.283
Cys	0.306	0.285
Cys	0.29	0.285
Cys	0.286	0.29
Cys	0.293	0.288
TA	0.374	0.263
TA	0.365	0.264
TA	0.355	0.262
TA	0.345	0.269
TA	0.35	0.273
C	0.361	0.075
C	0.346	0.081
C	0.333	0.086
C	0.33	0.096
C	0.32	0.086
DA	0.303	0.067
DA	0.293	0.071
DA	0.293	0.072
DA	0.298	0.08
DA	0.307	0.079
UA	0.55	0.058
UA	0.543	0.066
UA	0.542	0.069
UA	0.548	0.076
UA	0.556	0.077
TAA	0.157	0.549
TAA	0.148	0.549
TAA	0.143	0.543

TAA	0.153	0.545
TAA	0.161	0.542
MT	0.301	0.978
MT	0.29	0.98
MT	0.289	0.978
MT	0.299	0.978
MT	0.308	0.974
MO	0.241	0.732
MO	0.231	0.734
MO	0.229	0.731
MO	0.235	0.727
MO	0.244	0.724

Table S24 The training matrix of the colorimetric response patterns against the the antioxidants at 10 nM and other interfering species at 1μM using Zn-based nanozyme, Co-based nanozyme sensor assay.

Antioxidants and interfering species	A_0-A Zn-based nanozyme	A_0-A Co-based nanozyme
GSH	0.294	0.357
GSH	0.281	0.359
GSH	0.29	0.362
GSH	0.282	0.365
GSH	0.282	0.363
AA	0.409	0.29
AA	0.399	0.291
AA	0.403	0.287
AA	0.396	0.289
AA	0.402	0.286
Cys	0.301	0.283
Cys	0.287	0.285
Cys	0.309	0.285
Cys	0.292	0.29
Cys	0.303	0.288
TA	0.274	0.263
TA	0.265	0.264
TA	0.275	0.262
TA	0.267	0.269
TA	0.271	0.273
C	0.372	0.075
C	0.366	0.081
C	0.375	0.086
C	0.367	0.096
C	0.357	0.086
DA	0.345	0.067
DA	0.338	0.071
DA	0.347	0.072
DA	0.337	0.08
DA	0.343	0.079
UA	0.437	0.058
UA	0.428	0.066
UA	0.427	0.069
UA	0.416	0.076
UA	0.411	0.077
CA	0.409	0.594
CA	0.396	0.598
CA	0.413	0.601

CA	0.405	0.601
CA	0.407	0.602
GA	0.425	0.549
GA	0.417	0.547
GA	0.429	0.551
GA	0.426	0.552
GA	0.43	0.553
MT	0.38	0.418
MT	0.373	0.418
MT	0.391	0.415
MT	0.382	0.415
MT	0.382	0.415

Table S25 The training matrix of the colorimetric response patterns against the antioxidants at 10 nM in serum samples using Cu-based nanozyme, Co-based nanozyme sensor assay.

Antioxidants	A_0-A Cu-based nanozyme	A_0-A Co-based nanozyme
GSH	0.109	0.188
GSH	0.119	0.182
GSH	0.122	0.167
GSH	0.117	0.175
GSH	0.107	0.183
AA	0.054	0.249
AA	0.059	0.257
AA	0.071	0.245
AA	0.069	0.244
AA	0.061	0.248
Cys	0.186	0.202
Cys	0.194	0.197
Cys	0.197	0.189
Cys	0.194	0.196
Cys	0.189	0.201
TA	0.324	0.178
TA	0.326	0.173
TA	0.326	0.168
TA	0.323	0.177
TA	0.32	0.182
C	0.096	0.239
C	0.1	0.244
C	0.103	0.234
C	0.102	0.24
C	0.095	0.246
DA	0.166	0.148
DA	0.171	0.146
DA	0.173	0.134
DA	0.172	0.137
DA	0.168	0.142
UA	0.159	0.139
UA	0.16	0.131
UA	0.157	0.122
UA	0.153	0.129
UA	0.149	0.132

Table S26 The training matrix of the colorimetric response patterns against the antioxidants at 10 nM in serum samples using Fe-based nanozyme, Co-based nanozyme sensor assay.

Antioxidants	A_0-A Fe-based nanozyme	A_0-A Co-based nanozyme
GSH	0.227	0.188
GSH	0.225	0.182
GSH	0.229	0.167
GSH	0.23	0.175
GSH	0.227	0.183
AA	0.287	0.249
AA	0.285	0.257
AA	0.284	0.245
AA	0.284	0.244
AA	0.279	0.248
Cys	0.268	0.202
Cys	0.266	0.197
Cys	0.267	0.189
Cys	0.268	0.196
Cys	0.268	0.201
TA	0.343	0.178
TA	0.344	0.173
TA	0.346	0.168
TA	0.346	0.177
TA	0.342	0.182
C	0.041	0.239
C	0.04	0.244
C	0.044	0.234
C	0.047	0.24
C	0.04	0.246
DA	0.285	0.148
DA	0.285	0.146
DA	0.291	0.134
DA	0.286	0.137
DA	0.285	0.142
UA	0.341	0.139
UA	0.341	0.131
UA	0.341	0.122
UA	0.344	0.129
UA	0.331	0.132

Table S27 The training matrix of the colorimetric response patterns against the antioxidants at 10 nM in serum samples using Zn-based nanozyme, Co-based nanozyme sensor assay.

Antioxidants	A_0-A Zn-based nanozyme	A_0-A Co-based nanozyme
GSH	0.143	0.188
GSH	0.145	0.182
GSH	0.144	0.167
GSH	0.14	0.175
GSH	0.136	0.183
AA	0.083	0.249
AA	0.081	0.257
AA	0.086	0.245
AA	0.09	0.244
AA	0.086	0.248
Cys	0.206	0.202
Cys	0.205	0.197
Cys	0.219	0.189
Cys	0.209	0.196
Cys	0.203	0.201
TA	0.244	0.178
TA	0.24	0.173
TA	0.24	0.168
TA	0.238	0.177
TA	0.245	0.182
C	0.114	0.239
C	0.113	0.244
C	0.119	0.234
C	0.107	0.24
C	0.116	0.246
DA	0.146	0.148
DA	0.143	0.146
DA	0.144	0.134
DA	0.136	0.137
DA	0.152	0.142
UA	0.205	0.139
UA	0.206	0.131
UA	0.216	0.122
UA	0.205	0.129
UA	0.212	0.132

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