Supporting Information

Preparation of a laccase mimicking nanozyme and its catalytic oxidation of phenolic pollutants

Xiaojian Xu,[a] Jinghui Wang,[a] Renliang Huang,[b,*] Wei Qi,[a,c] Rongxin Su,[a,b,c] Zhimin He[a]

[a] State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P.R. China

[b] School of Marine Science and Technology, Tianjin University, Tianjin 300072, P.R. China

[c] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin University, Tianjin 300072, P.R. China

---

* Author to whom correspondence should be addressed:

tjuhrl@tju.edu.cn (R.H.)

1. Supplementary Figures

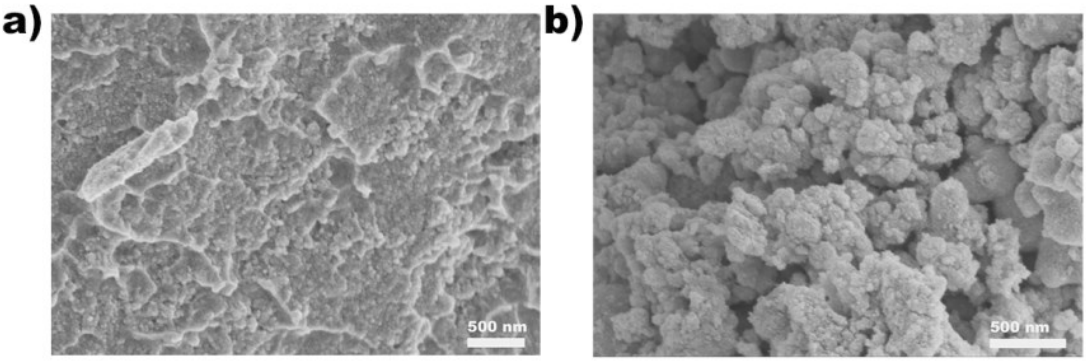


Figure S1. (a) SEM image of CP-Cu nanozymes, (b) SEM image of CT-Cu nanozymes

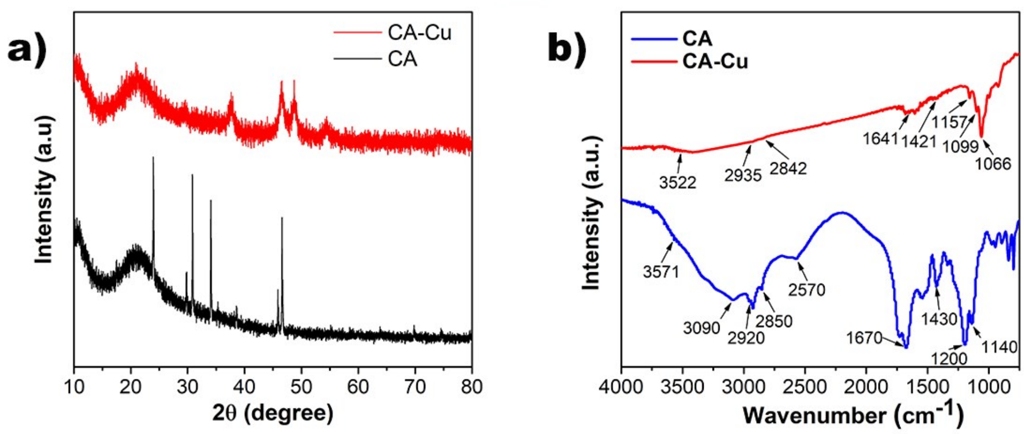


Figure S2. (a) XRD patterns and (b) FTIR spectra of CA-Cu nanozymes and Cys-Asp dipeptide

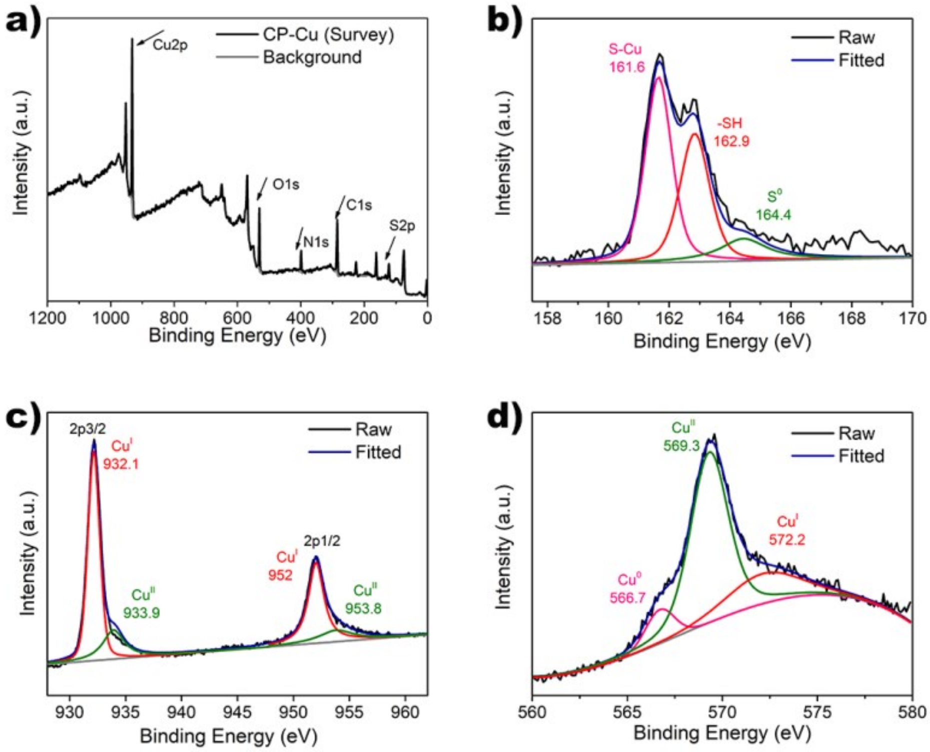


Figure S3. For CP-Cu nanozymes: (a) XPS fully scanned spectrum, (b) S 2p XPS spectrum, (c) Cu 2p XPS spectrum, (d) Cu LMM Auger spectrum

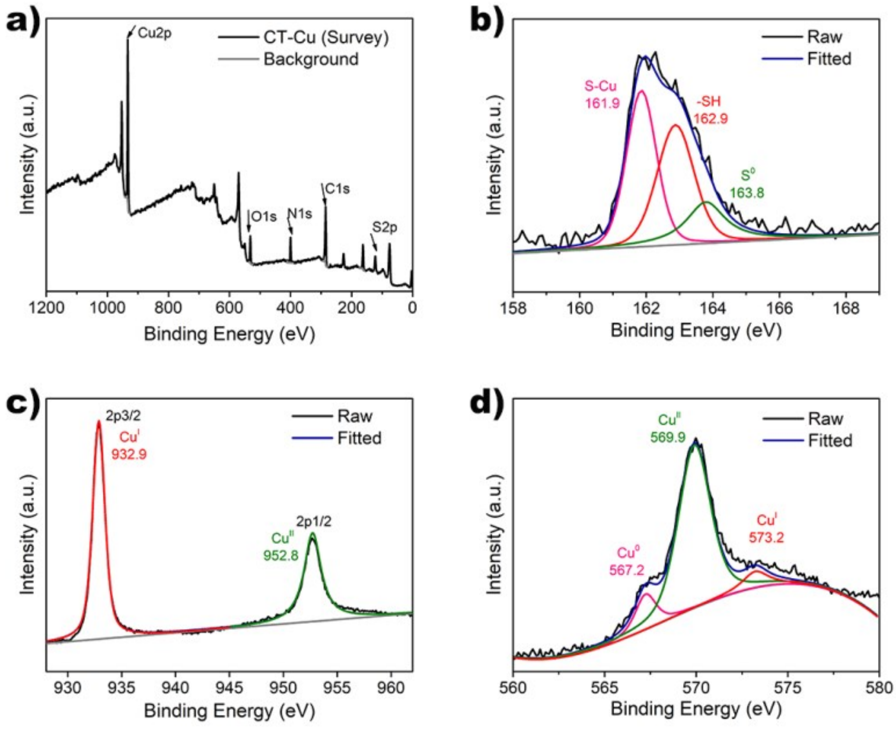
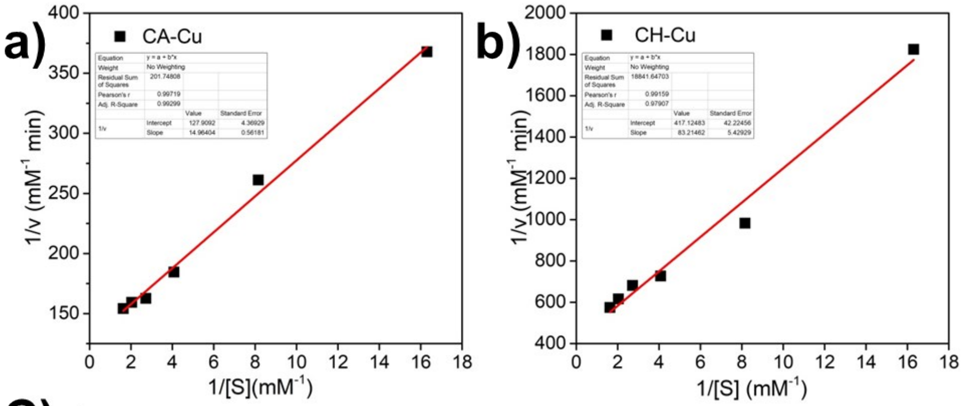


Figure S4. For CT-Cu nanozymes: (a) XPS fully scanned spectrum, (b) S 2p XPS spectrum, (c) Cu 2p XPS spectrum, (d) Cu LMM Auger spectrum



C)

Catalyst	ρ_e (g/L)	$[E]$ (mM)	K_m (mM)	v_{max} (mM min^{-1})	k_{cat} (min^{-1})	k_{cat}/K_m (mM^{-1} min^{-1})
CA-Cu	0.1	2.95×10^{-7}	0.12	7.82×10^{-3}	2.65×10^{4}	2.21×10^{5}
Laccase	0.1	1.55×10^{-3}	0.41	6.41×10^{-3}	4.13	10.07

Figure S5. (a) Lineweaver-Burk plot for CA-Cu nanozymes oxidizing 2,4-DP, (b) Lineweaver-Burk plot for CH-Cu nanozymes oxidizing 2,4-DP, (c) Kinetic parameters for CA-Cu and laccase.

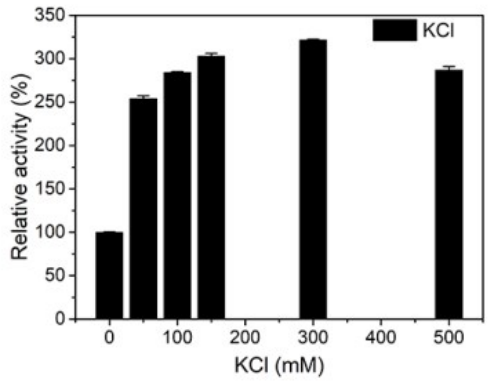


Figure S6. Effect of KCl at different concentrations

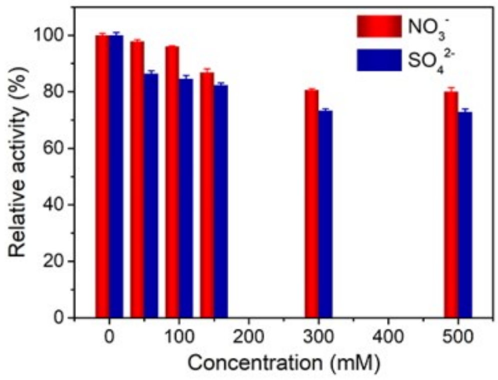


Figure S7. Catalytic performance of CA-Cu nanozymes with different concentrations of NO_3^- or SO_4^{2-}

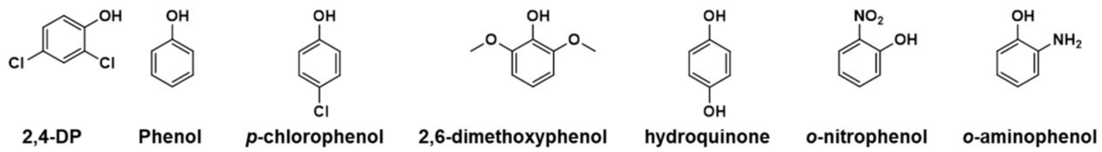


Figure S8. Molecular structures of six phenolic compounds.

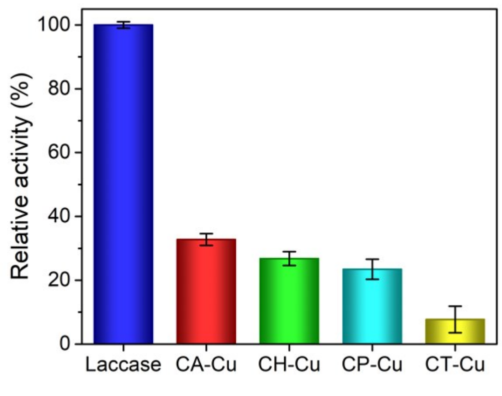


Figure S9. Comparison of catalytic activity of laccase and nanozymes with the same mass concentrations of copper.

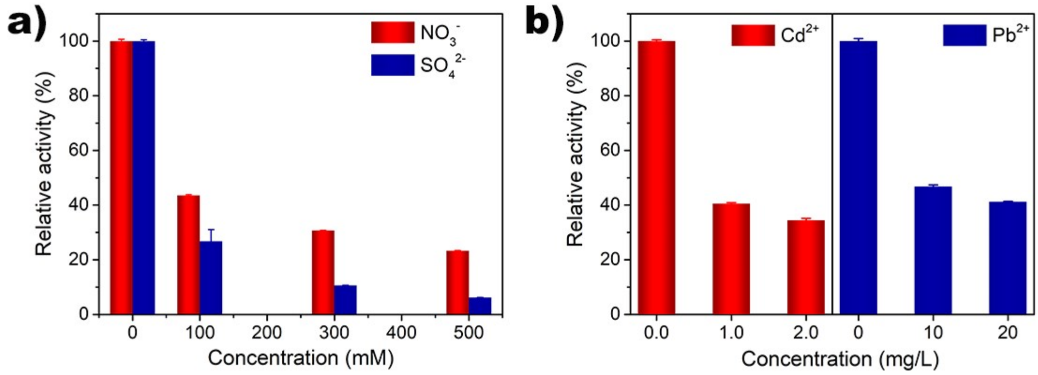


Figure S10. Catalytic performance of laccase with various ions (a) NO_3^- or SO_4^{2-}, (b) Heavy metal ions

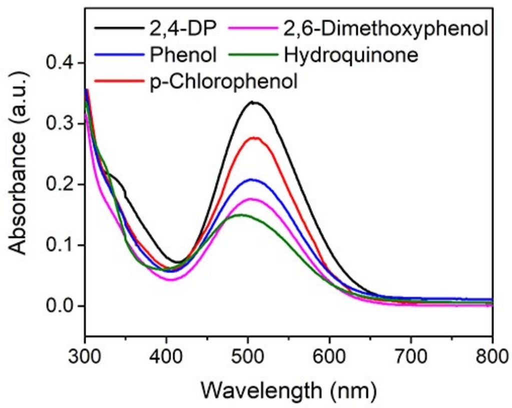


Figure 11. UV−vis spectra of the reaction product in the presence of laccase (pH 6.8 MES buffer, 0.1 mg/mL of laccase).

2. Supplementary Tables

Table S1. Hydrodynamic diameter (DLS) and zeta potential of different nanozymes in MES buffer, CA-Cu in MES buffer with different concentrations of substances.

Sample	Concentration/(mM/mg)	Diameter/nm	ζ-potential/mV
CA-Cu		1039.5	-14.2
CH-Cu		945.2	-7.7
CP-Cu		1089	-11.6
CT-Cu		1556	-10.6
CA-Cu (NaCl)	500	823.9	-17.6
CA-Cu (KCl)	500	843.2	-16.8
CA-Cu (NO^{3-})	500	865.8	-9.8
CA-Cu (SO_4^{2-})	500	1159	-10.5
CA-Cu ($Pb^{2+)}$	20	994.1	-8.3
CA-Cu (Cd^{2+})	2	849.7	-13.2

Table S2. Summary of FT-IR peaks of CA-Cu nanozyme and Cys-Asp dipeptide.

Chemical bond	CA-Cu nanozyme/cm^{-1}	Cys-Asp dipeptide/cm^{-1}
$\nu(-NH_2)$	3522	3571
$\nu(C=O)$	1641	1670
$\nu(C-N)$	1157	1200
$\nu(-OH)$	2841	2920
$\nu(C-H)$	2935	3090
$\nu(-SH)$	2324	2570

Table S3. XPS peak table of nanozymes.

Nannozyme	Item	Represent	Peak binding energy eV	Atomic %
CA-Cu	XPS full scan spectrum	S 2p	161.81	8.69
		C 1s	284.8	39.16
		N 1s	399.44	4
		O 1s	531.47	30.78
		Cu 2p	932.61	17.37
	S 2p XPS spectrum	S-Cu	161.6	50.19
		-SH	162.9	39.09
		S^0	164.4	10.72
	Cu 2p XPS spectrum	$Cu^I 2p3/2$	932.1	34.34
		$Cu^{II} 2p3/2$	933.9	30.33
		$Cu^I 2p1/2$	952	19.68
		$Cu^{II} 2p1/2$	953.8	15.64
	Cu LMM Auger spectrum	Cu^0	566.6	15.09
		Cu^I	569.2	64.16
		Cu^{II}	572.1	20.75
	XPS full scan spectrum	S 2p	161.21	10.38
		C 1s	284.8	50.89

		N 1s	400.11	12.20
		O 1s	531.69	9.56
		Cu 2p	932.85	16.97
CP-Cu	S 2p XPS spectrum	S-Cu	161.6	51.00
		-SH	162.9	8.88
		S^0	164.4	40.12
	Cu 2p XPS spectrum	$Cu^I 2p3/2$	932.1	45.89
		$Cu^{II} 2p3/2$	933.9	14.77
		$Cu^I 2p1/2$	952	29.61
		$Cu^{II} 2p1/2$	953.8	9.73
	Cu LMM Auger spectrum	Cu^0	566.7	8.89
		Cu^I	569.3	68.80
		Cu^{II}	572.2	22.31
	XPS full scan spectrum	S 2p	161.78	9.79
		C 1s	284.8	45.18
		N 1s	399.39	10.16
		O 1s	530.91	18.26
		Cu 2p	932.17	16.31

CT-Cu	S 2p XPS spectrum	S-Cu	161.9	41.19
		-SH	162.9	39.59
		S^0	163.8	19.22
	Cu 2p XPS spectrum	Cu^I2p3/2	932.9	59.70
		Cu^I2p1/2	952.8	40.30
	Cu LMM Auger spectrum	Cu^0	567.2	12.87
		Cu^I	569.9	79.94
		Cu^{II}	573.2	7.19