Supporting Information

Noble metal-enhanced Au@CuO heterostructure with multienzyme-mimicking activities for colorimetric detection of tannic acid

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Experimental section

Materials. Cupric chloride ($CuCl_2$), poly(vinylpyrrolidone) (PVP, MW = 40000), sodium hydroxide (NaOH) 3,3′,5,5′-tetramethylbenzidine (TMB), hydrogen peroxide (H_2O_2), gold(III) chloride trihydrate ($HAuCl_4•3H_2O$), terephthalic acid (TA), 10-Anthracenediyl-bis(methylene)(ABDA), o-phenylenediamine(OPD), 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulfonate) (ABTS), reduced glutathione (GSH, 97%), rhodamine B (Rh B), 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) were purchased from Sigma-Aldrich. All the above materials were of reagent grade and used as received without further purification.

Synthesis of Au@CuO Nc. The preparation of Cu_2O nanocubes began by adding a $CuCl_2$ aqueous solution (33 mL, 3.20 mM) to a 50 mL vial. Subsequently, a NaOH aqueous solution (1 mL, 0.35 M) was introduced gradually under magnetic stirring, causing the solution to shift from colorless to light blue. Five minutes later, a quick injection of L-ascorbic acid sodium aqueous solution (1 mL, 0.10 M) into the mixture was performed, and the reaction was allowed to continue for 30 minutes during which the color transitioned from light blue to orange, signaling the formation of Cu_2O. The resultant Cu_2O nanocubes were then isolated by centrifugation and cleansed with a mixture of DI water and ethanol. For the synthesis of Au@CuO Nc, these Cu_2O nanocubes were redissolved in deionized water (10 mL). PVP (0.10 g) was added until it dissolved completely, followed by the addition of $HAuCl_4$ (0.2 mL, 24 mM). The mixture was stirred magnetically at 25 ℃ for 1 hour. The final product, Au@CuO Nc, was gathered through centrifugation and repeatedly washed with a DI water/ethanol solution.

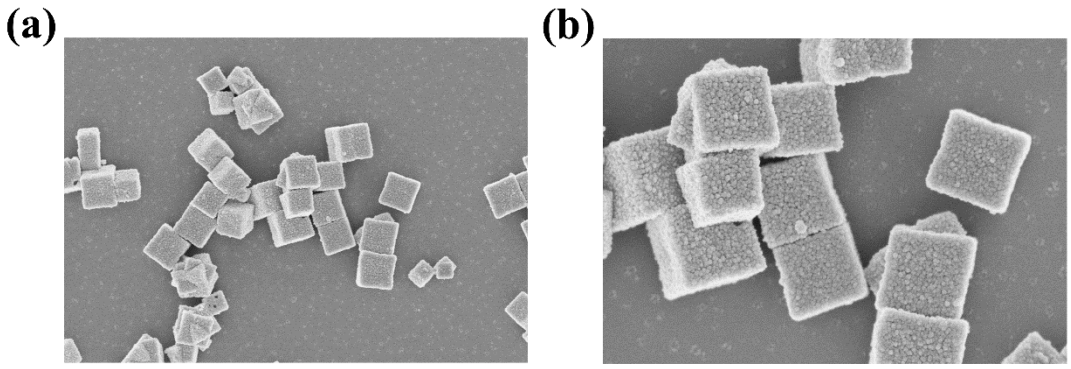

Fig. S1. (a, b) SEM images of Au@CuO

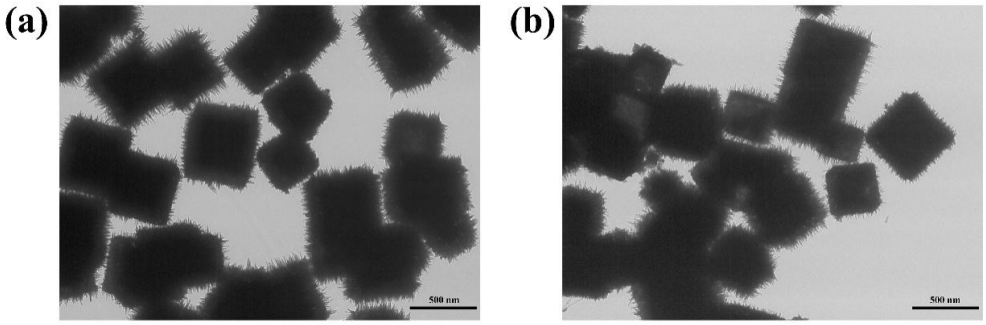

Fig. S2. (a, b) TEM images of Au@CuO.

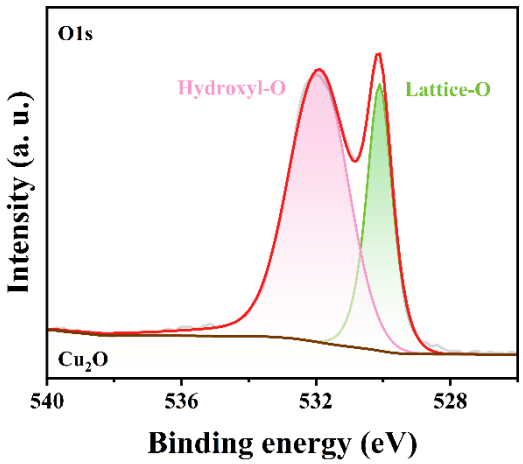

Fig. S3. O 1s XPS spectra of Cu_2O.

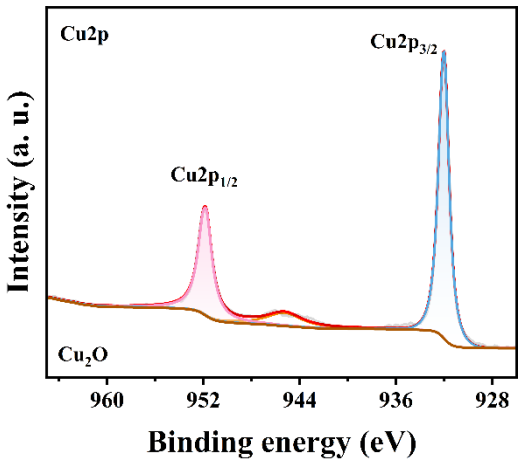

Fig. S4. Cu2p XPS spectra of Cu_2O.

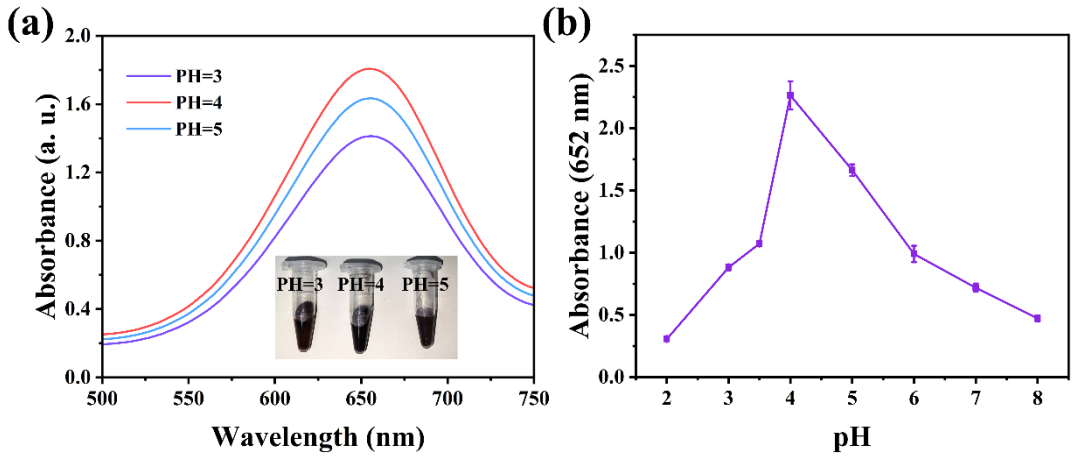

Fig. S5. (a) the color and curve of ABTS + H2O2 + Au@CuO; (b) the color and curve of OPD + H2O2 + Au@CuO

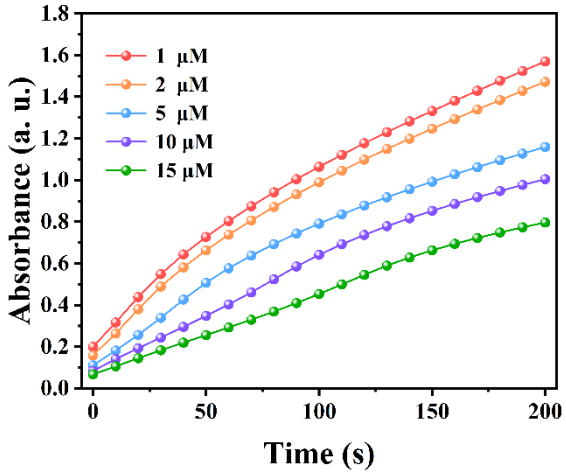

Fig. S6. The change in absorbance for difference concentrations of TA over time**.**

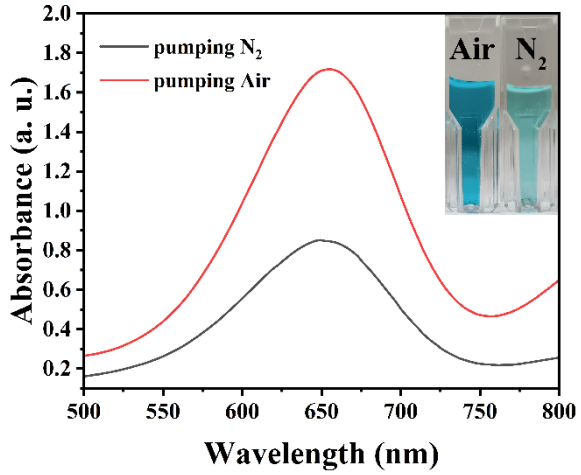

Fig. S7. Changes in color and absorbance under different conditions**.**

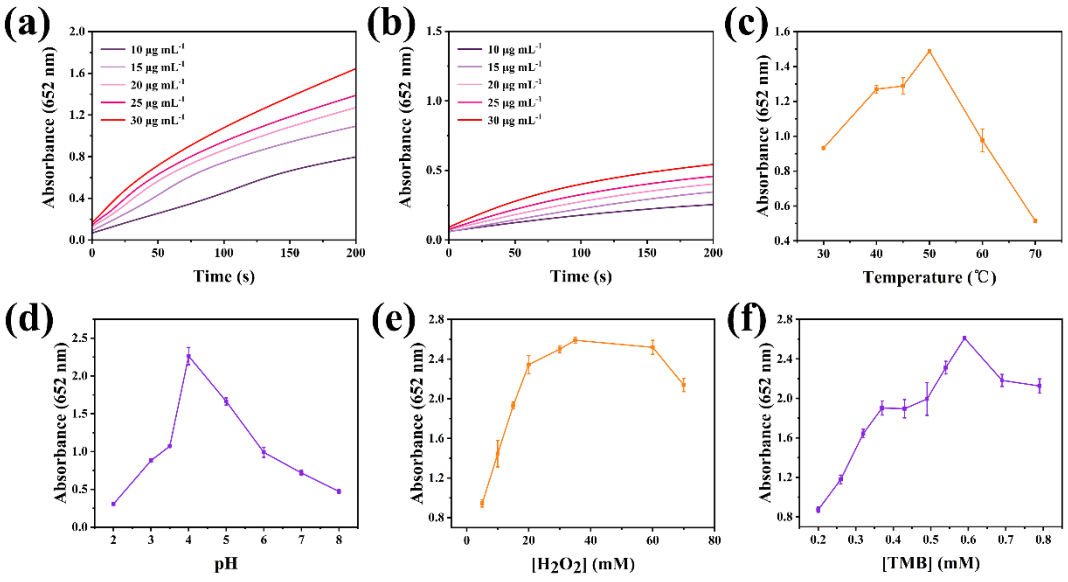

Fig. S8. (a, b) Time-dependent absorbance at 652 nm varied with different concentrations of Au@CuO and Cu2O; Effect of various factors on the peroxidase-like property of Au@CuO nanozymes: (c) Temperature, (d) pH, (e) H2O2 concentration, and (f) TMB concentration.

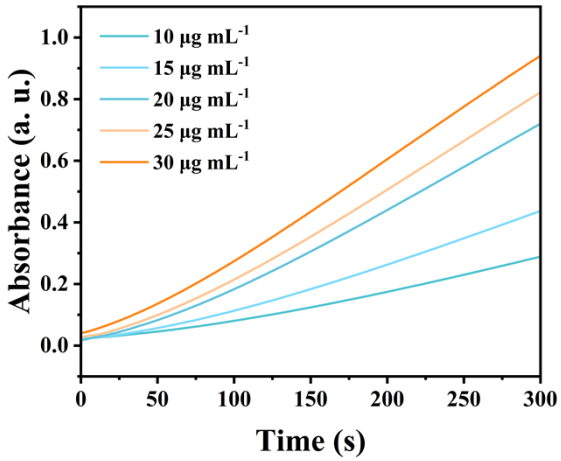

Fig. S9. Time-dependent absorbance at 420 nm varied with different concentrations of Au@CuO when using OPD as the reaction substrate.

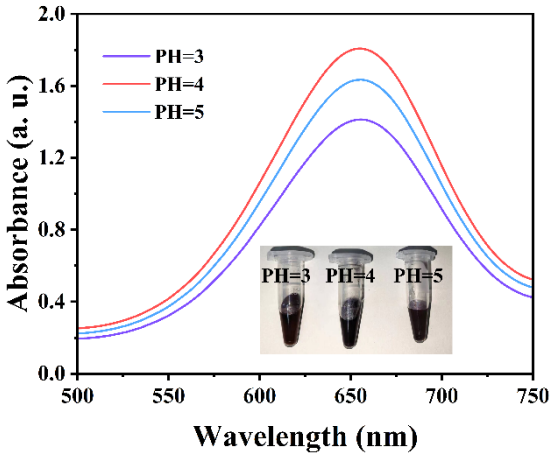

Fig. S10. Different pH conditions on the activity of nanomaterials.

Table S1. Comparison of the kinetic constants of different nanozymes.

catalyst	substance	K_m(mM)	Vmax(10^{-8}M/s)	refs
pd@CeO_2/N-PC-rGO	TMB	0.207	15.1	[1]
	H_2O_2	0.605	6.75	
KCN-8	TMB	0.035	4.62	[2]
	H_2O_2	1.05	4.29	
0.2-Cu-N/C	TMB	72.8	0.255	[3]
	H_2O_2	0.53	1.42	
Cu NPs/CoO/CNFs	TMB	0.26	12.32	[4]
	H_2O_2	0.14	42.24	
PAN-CuO	TMB	0.58	20.14	[5]
	H_2O_2	0.09	4.68	
UiO-66-NH_2-Pt	TMB	0.322	16.49	[6]
	H_2O_2	1.25	0.232	
Au/Cu_2O	TMB	0.21	6.08	[4]
	H_2O_2	10.56	6.68	
UsAuNPs/2D MOF	TMB	0.14	5.21	[7]
	H_2O_2	0.05	13.48	
Au@CuO	TMB	0.52	51.49	this work
	H_2O_2	6.35	24.86	

Table S2. Comparison of Nanoparticle-Based Detection of TA.

No.	Material	Linear range (μM)	LOD (μM)	Ref.
1	SWNTs	0.05-1	0.008	[8]
2	$K3Fe(CN)_6$	0.0003-0.1	0.0001	[9]
3	$KMnO_4$/Ce(IV)	0.07-7	0.026	[10]
4	PEG/CPE	0.08-2.1	0.072	[11]
5	ZnO-Pt/GCE	0.04-31.56	0.02	[12]
6	Cu/CN	0.09-3.2	0.03	[13]
7	Fe-N-C MFs	0.2-50	0.079	[14]
8	Au@CuO	0.3-2.4	0.25	this work

Table S3. Detection results of TA in actual sample.

Samples	Concentration (μM)		Recovery	RSD
	Added	Found	%	%
Green tea	0.5	0.6676	96.62	3.59
	1.0	1.1320	94.75	4.82
	2.0	2.1861	100.08	2.01

Notes and references

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