Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Bimetal loaded graphitic carbon nitride with synergistic enhanced peroxidase-like activity for colorimetric detection of p-phenylenediamine

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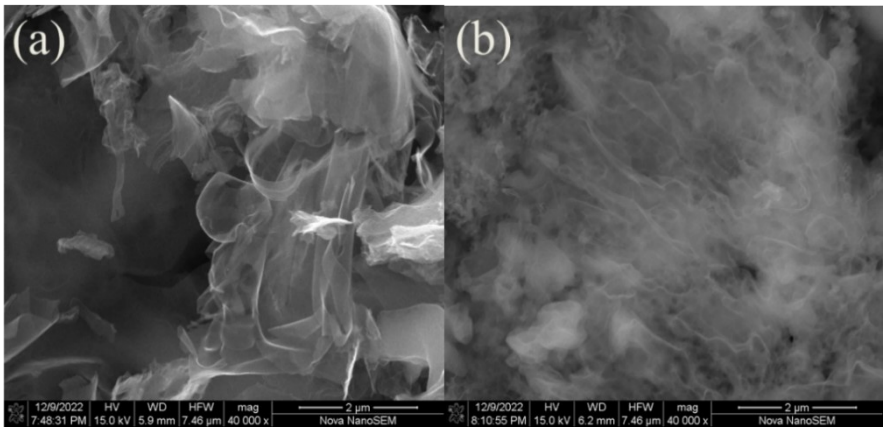

Fig. S1 (a) SEM of pristine CN and (b) Fe/Ni-CN.

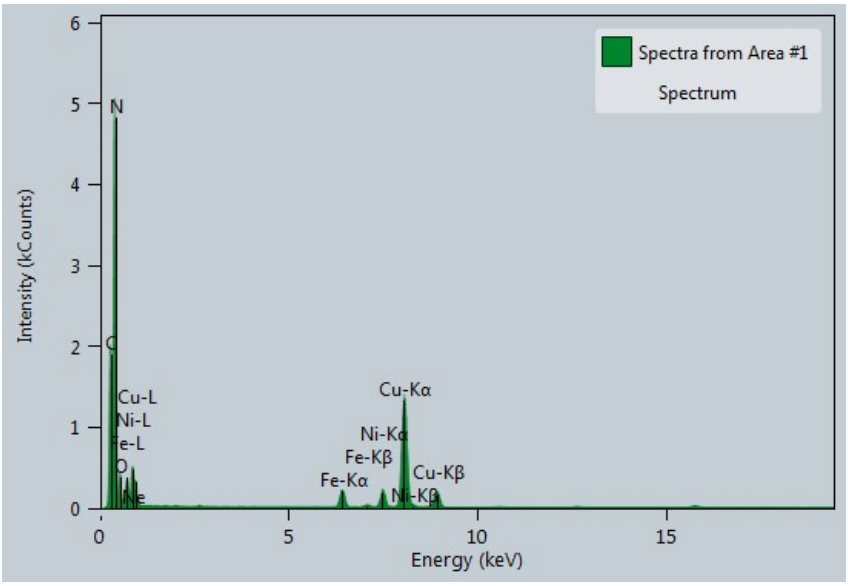

Fig. S2 EDS spectrum of Fe/Ni-CN.

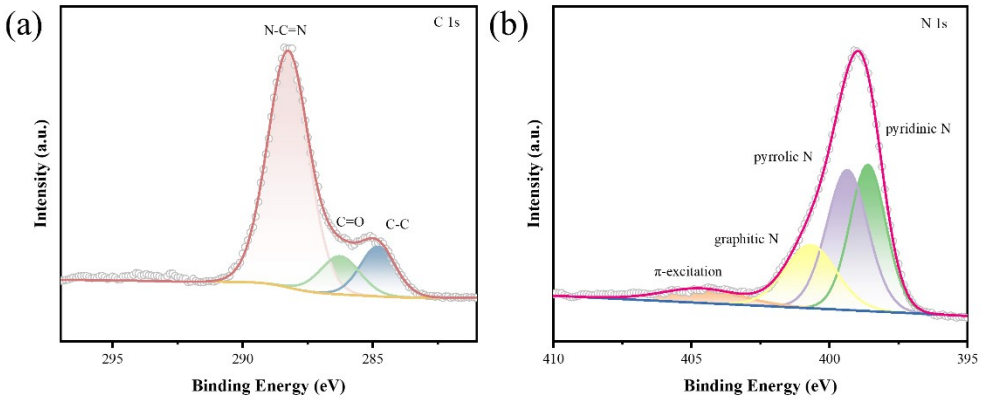

Fig. S3 XPS spectra of C 1s (a) and N 1s (b).

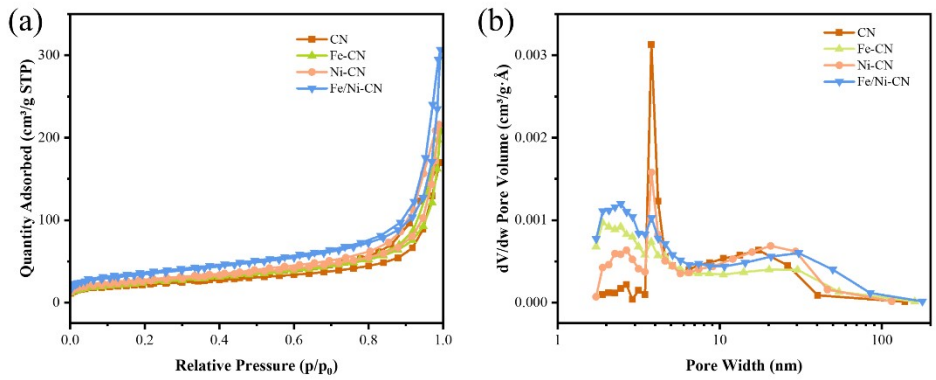

Fig. S4 (a) N_2 adsorption/desorption isotherms of CN, Fe-CN, Ni-CN and Fe/Ni-CN and (b) the corresponding pore-size distribution curves.

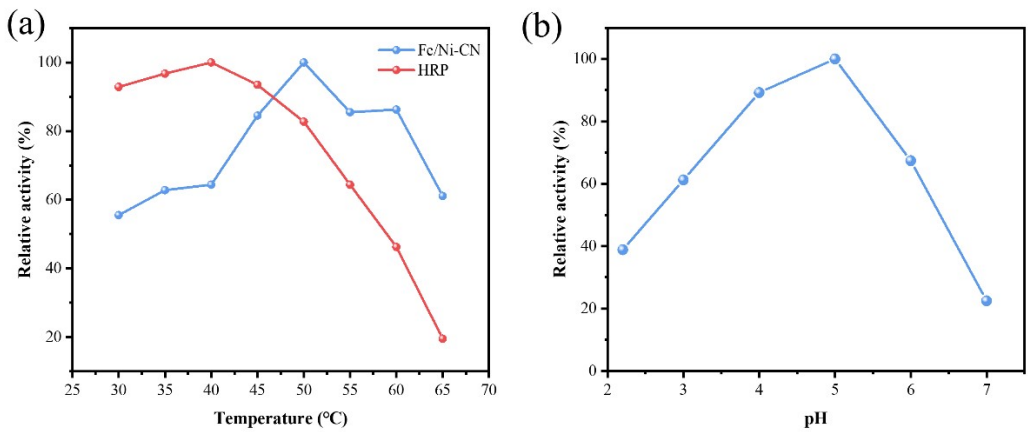

Fig. S5 (a) Comparison of Fe/Ni-CN and HRP under varying temperature, (b) The influence of pH on the catalytic activity of Fe/Ni-CN.

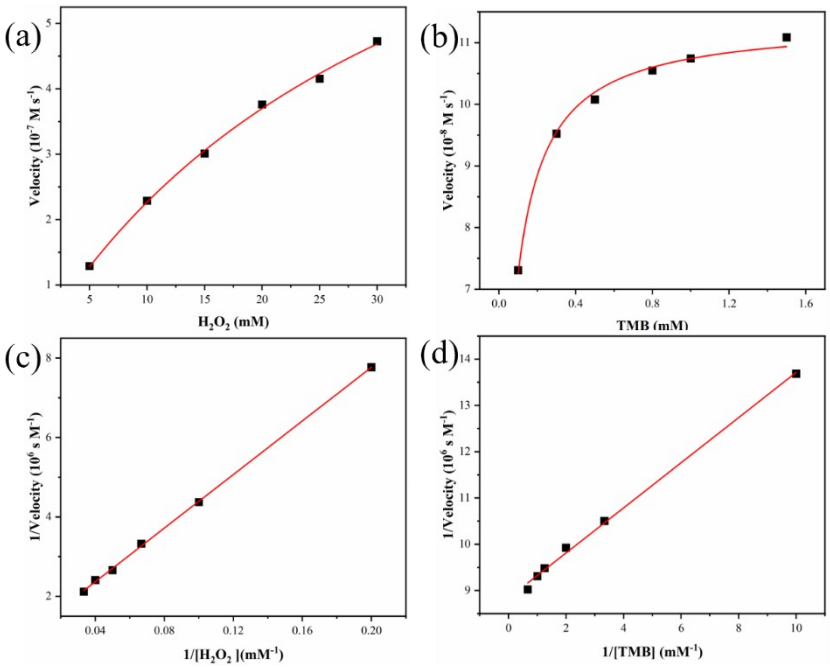

Fig. S6 Steady-state kinetics of Fe-CN nanozyme. (a and b) Michaelis–Menten curves fit for varied concentrations of H_2O_2 with fixed concentration of TMB, and varied concentrations of TMB with fixed concentration of H_2O_2. The Lineweaver–Burk plots for various concentrations of (c) H_2O_2 and (d) TMB.

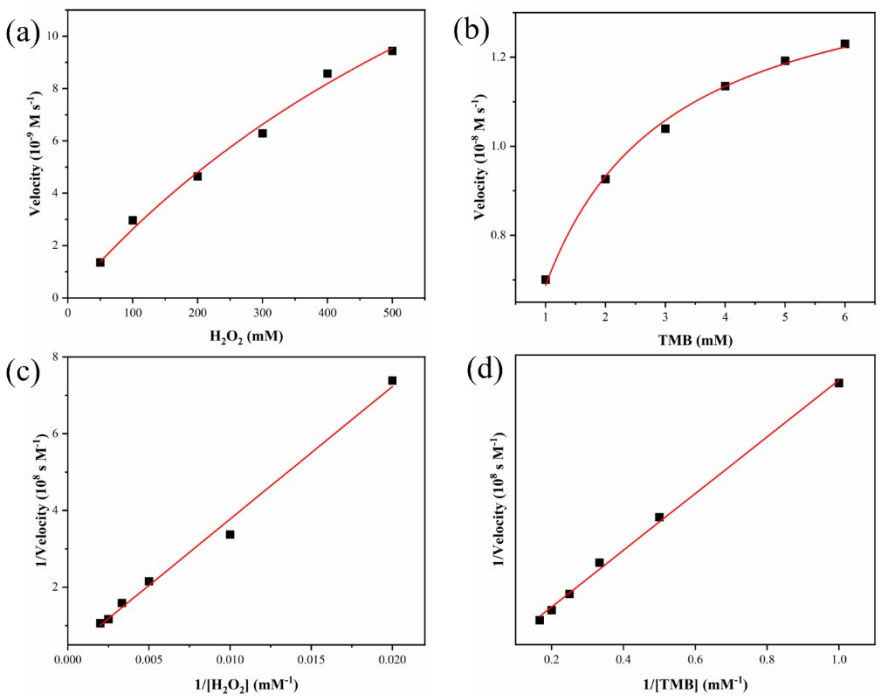

Fig. S7 Steady-state kinetics of Ni-CN nanozyme. (a and b) Michaelis–Menten curves fit for varied concentrations of H_2O_2 with fixed concentration of TMB, and varied concentrations of TMB with fixed concentration of H_2O_2. The Lineweaver–Burk plots for various concentrations of (c) H_2O_2 and (d) TMB.

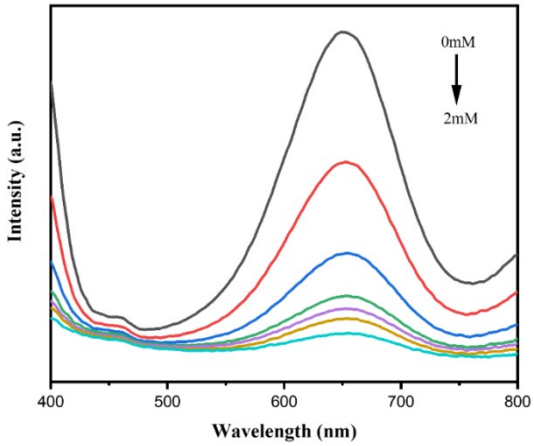

Fig. S8 The effect of •OH scavenger thiourea with different concentrations on the absorbance of TMB + H_2O_2 + Fe/Ni-CN reaction system.

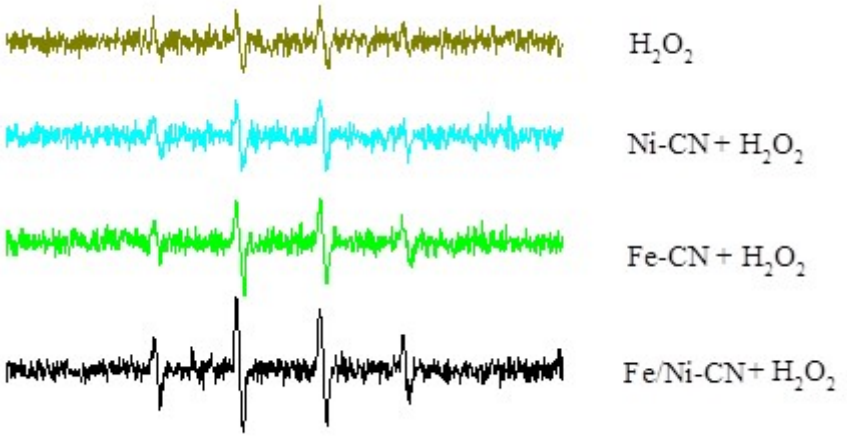

Fig. S9 The effects of Fe-CN, Ni-CN and Fe/Ni-CN on the formation of hydroxyl radical detected by ESR.

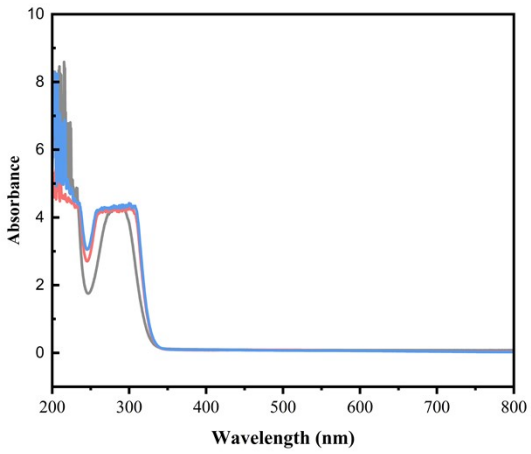

Fig. S10 The absorption spectra of dyed hair extract solutions with addition of TMB/H_2O_2. (blue: blank , red: hair dye 1, gray: hair dye 2).

Table S1. BET surface areas and pore volumes of catalysts.

Samples	S_{BET} (m^2/g)	pore volume (cm^3/g)
CN	76.04	0.2571
Ni-CN	91.61	0.3245
Fe-CN	86.32	0.3156
Fe/Ni-CN	121.86	0.4611

Table S2. Comparison of kinetic parameters of different nanozymes.

Nanozyme	[E] μg/ml	Substrate	K_m (mM)	V_{max} (M s^{-1})	Reference
Fe/Ni-CN	10	TMB	0.052	7.43×10^{-8}	This work
		H_2O_2	6.350	17.60×10^{-8}	
Fe-CN	10	TMB	0.066	7.36×10^{-8}	
		H_2O_2	33.15	9.82×10^{-8}	
Ni-CN	10	TMB	1.05	1.43×10^{-8}	
		H_2O_2	422	3.1×10^{-8}	
Cu NPs/g-C_3N_4	150	TMB	0.389	5.84×10^{-7}	1
		H_2O_2	9.270	3.84×10^{-7}	
MIL-101(Fe)	20	TMB	0.585	10.038×10^{-8}	2
		H_2O_2	0.043	5.138×10^{-8}	
Co-g-C_3N_4-2	100	TMB	0.113	8.64×10^{-8}	3
		H_2O_2	318.58	9.46×10^{-8}	
MoS_2@CNNS(30)	120	TMB	0.117	3.03×10^{-8}	4
		H_2O_2	0.602	3.15×10^{-8}	
Fe_3O_4	40	TMB	0.098	3.44×10^{-8}	5
		H_2O_2	154	9.78×10^{-8}	
PMCS	100	TMB	0.224	12.66×10^{-8}	6
		H_2O_2	40.160	12.15×10^{-8}	
HRP	1×10^{-3}	TMB	0.430	10×10^{-8}	7
		H_2O_2	3.700	8.70×10^{-8}	

Table S3. Calculated energies of the reaction pathway for different catalysts.

Free energy(ev) / nanozyme	$E_{b,1}$	$E_{b,2}$	$E_{b,3}$	$E_{b,4}$	$E_{b,5}$
Fe/Ni-CN	0.35	-2.23	-1.77	-2.71	-3.59
Fe-CN	0.64	-2.67	-1.88	-2.86	-3.59
Ni-CN	0.77	-2.95	-1.97	-3.05	-3.59

Table S4. Comparison of the proposed method with other reports for the detection of PPD

Materials	Method	Linear Rang (μM)	LOD (μM)	Reference
Fe/Ni-CN	Colorimetry	0.2-30	0.02	This work
ZnBNC	Colorimetry	0.3-10	0.11	[8]
Fe_3O_4/N-GQDs	Colorimetry	2-70	0.53	[9]
Fe–SAs@FNC	Colorimetry	0.2-50	0.07	[10]
CDs@NBD	Fluorescence	0.1-10	0.056	[11]
HRP/NPG/GE	ECL	2-170	0.33	[12]
S-PPD-DCM	Fluorescence	0.09-9	0.05	[13]

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