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Reusable nickel foam supported 3D hierarchical Co-Fe-Ni mixed metal oxides with peroxidase-like activity as biosensor for colorimetric detection of H_2O_2 †

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Supplementary information:

Regents and materials. Nickel nitrate ($Ni(NO_3)_2·6H_2O$), Iron nitrate ($Fe(NO_3)_3·9H_2O$), Cobalt nitrate ($Co(NO_3)_2·6H_2O$), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), and 3,3,5,5−Tetramethylbenzidine (TMB·2HCl) were purchased from Macklin (Shanghai, China). Humic acid, Glucose, Urea, Arginine, Sodium dodecyl sulfate (SDS), Hydrogen peroxide (30%, H_2O_2) was bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ni foam was purchased from Kunshan Guangjiayuan New Materials Co., Ltd (Kunshan, China). All of reagents are analytical grade and used directly without any further purification. Ultrapure water used throughout the experiment was prepared by the floc water purification system.

Characterization. The crystallinity of the products was analyzed by Rigaku D/Max2500PC powder X−ray diffractometer with Cu Kα radiation (Rigaku, Japan, U = 40 kV, I = 40 mA, and 2θ = 5–80°). The morphology and composition of the samples were verified by scanning electron microscopy (FEI APREO, America) equipped with energy-dispersive X-ray spectroscopy (EDS) under a 200 kV accelerating voltage. The surface elemental composition and valence analysis were performed on X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi). All of the XPS spectra were calibrated to the C 1s peak of adventitious carbon (284.8 eV). The electron spin resonance (ESR) spectra were carried out using a Bruker ESP−300E ESR spectrometer at room temperature (Bruker, Germany). UV−vis absorption spectra were obtained on a UV−8000PC spectrophotometer (Puxi, China).

Table S1. Experimental conditions of different experiment

Experiment name	C_{TMB}(mM)	$C_{H_2O_2}$(mM)	t (℃)	pH
pH effect	1	250	30	3-8
Temperature effect	1	250	25-60	4.17
kinetic experiment (1)	0.05-0.75	250	30	4.17
kinetic experiment (2)	1	1-60	30	4.17

Table S2. Kinetic parameters (K_m and V_{max}) of various nanozymes.

Nanozymes	K_m/mM		$V_{max}/10^{-8}Ms^{-1}$		Ref.
	TMB	H_2O_2	TMB	H_2O_2	
Co/Fe-NiO@NF	0.213	12.130	9.360	9.710	This work
HRP	0.434	3.700	10.00	8.710	[1]
Ni-MOF	0.365	2.490	6.530	130.0	[2]
N-doped graphene/$ZnFe_2O_4$	0.907	115.520	9.710	7.440	[3]
Au/CeO_2 CSNPs	0.290	44.69	3.900	2.230	[4]
Cu NCs	0.648	29.16	5.96	4.22	[5]
Cu-Ag/rGO	0.85	20.93	3.82	6.23	[6]

Table S3. Various methods for H_2O_2 detection.

Detection Method	Sensor Type	Linear Range	Detection Limit	Ref.
Colorimetry	$Ce/ZnCo_2O_4$	0.2-1 mM	175 μM	[7]
Colorimetry	GO-FeTPyP	0.02-0.5 mM	72 μM	[8]
Colorimetry	GA-AgNP	1-8 mM	340 μM	[9]
Colorimetry	$Co_3O_4/BiPc(OC_8H_9)_{12}$	3-20 mM	350 μM	[10]
Colorimetry	CDs@ZIF-8	0.1-1 mM	3.6 μM	[11]
Electrochemical method	MnO_2-NWs@Au-NPs/GF	0.01-9.5 mM	1.9 μM	[12]
Electrochemical method	ITO-rGO-AuNPs	0.025-3 mM	6.5 μM	[13]
Fluorescence	MoO_xQDs@Co/Zn-MOFs	2-150 μM	32.6 pmol	[14]
High performance liquid chromatography	------	------	0.1 μM	[15]
Colorimetry	Co/Fe-NiO@NF	0.2-4 mM	32.9 μM	This work

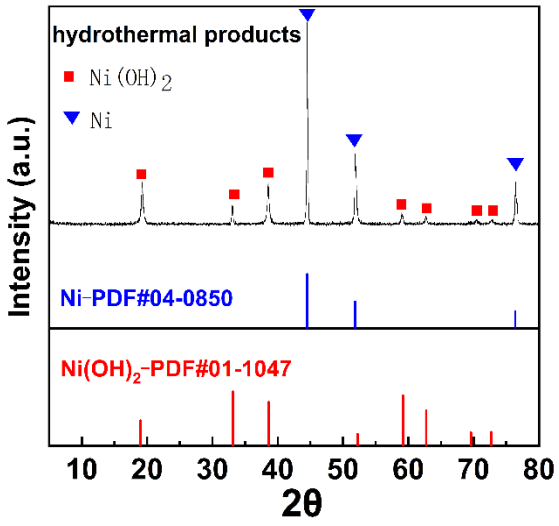

Figure S1. XRD spectra of the sample before calcination.

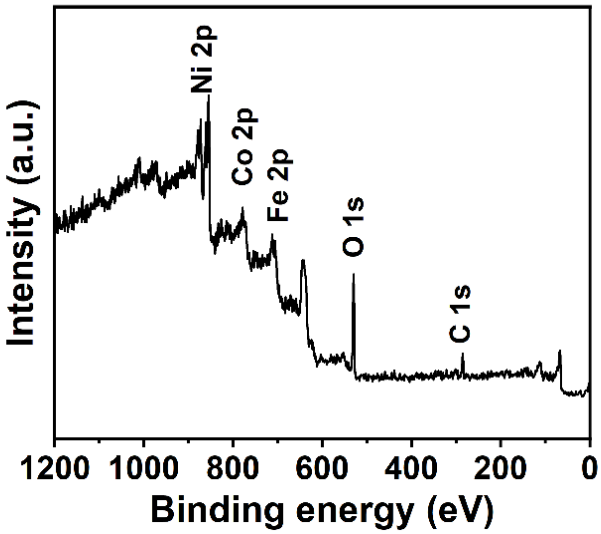

Figure S2. Survey XPS spectra of Co/Fe-NiO@NF

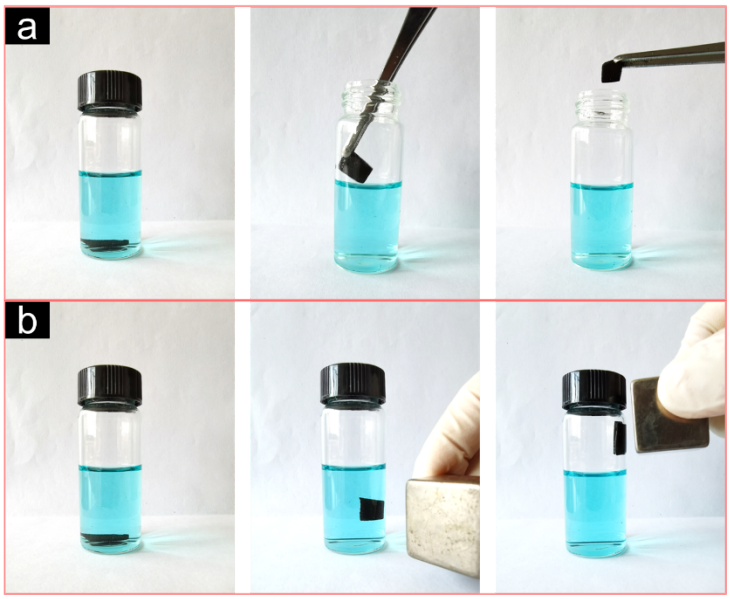

Figure S3. Easy separation of Co/Fe-NiO@NF by tweezers (a) and magnet (b).

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