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Reasonable construction of a bimetallic organic framework MIL-88B (Fe, Ni) nanoenzyme based on deep learning assisted doxycycline hydrochloride and methyloxytetracycline hydrochloride

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Experimental Section

Chemicals and Materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), terephthalic acid ($C_8H_6O_4$, TA), dimethyl sulfoxide (DMSO), p-benzoquinone (PBQ), sodium azide (NaN_3) and 30% H_2O_2 were purchased from McLean Biochemical Technology Co. Ltd.(http://macklin.cn.qianyan.biz/);3,3', 5,5' -Tetramethylbenzidine (TMB) and 2,2 '- diazobis-3-ethylbenzothiazolin-6-sulfonic acid (ABTS) were purchased from Shanghai Ruien Biotechnology Co. Ltd.(http://ruien.company.lookchem.cn/); O-phenylenediamine (OPD), sodium hydroxide (NaOH), thiourea (TH), ethylenediaminetetraacetic acid (EDTA), and N, N-dimethylformamide (DMF) were purchased from Chengdu Cologne Chemical Co. Ltd(http://www.cdkelong.com/); Beef extract and peptone purchased from Beijing Aoboxing Biotechnology Co. Ltd.(http://bjabxing.foodmate.net/); Agar from Aladdin(https://www.aladdin-e.com/); All experimental water was deionized (18.25 M Ω · cm); The reagents used in the experiment are all analytical pure and have not been further processed.

Characterizations

The crystal structure, morphological structure, and elemental composition were analyzed using X-ray diffraction (Dandong, China, DX-2700), transmission electron microscopy (JSM4800F, JOEL, Japan), scanning electron microscopy (JOEL-2100 F, Japan), TEM mapping, and X-ray photoelectron spectroscopy (XPS, ESCALAB-250Xi, China), respectively. The acidity and alkalinity of the solution were measured

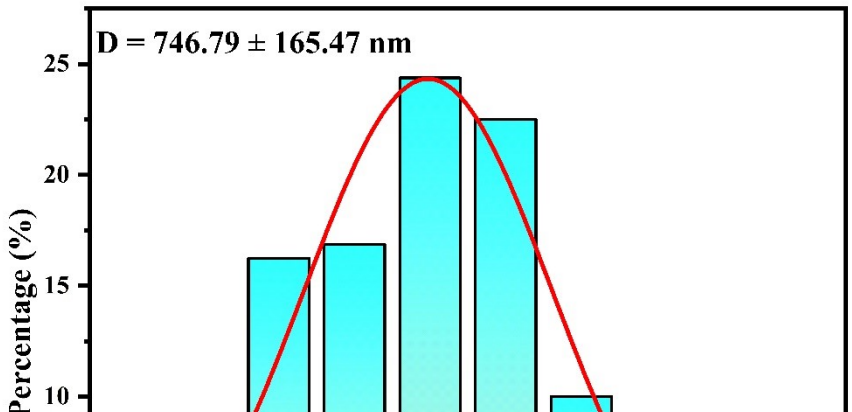
by the FE-28 pH meter (Met Toledo International Trade (Shanghai) Co. Ltd.). Record the Fourier transform infrared spectrum using Bruker VERTEX 70. The absorbance measurement is carried out on the Spectrum 210 Plus spectrophotometer.

DFT calculation details

Spin-polarized first-principle calculation was performed in the framework of density functional theory as implemented in the VASP program[1].The generalized gradient approximation of Perdew-Burke-Enzerh was employed for the electronic exchange and correlation. The plane wave pseudopotential with a kinetic cutoff energy of 450 eV within the projector augmented wave (PAW) method was used[2, 3]. The self-consistent the total energy convergence criteria were less than 10^{-4} eV and the geometry optimization was terminated when the forces on all atoms were smaller than 0.02 eV $Å^{-1}$. K-point was generated by the Monkhorst-Pack grid method with 2 × 2× 1[4, 5] for geometry optimization. The free energy was calculated using the Eq. 1:

$$G = E + ZPE + TS \quad [1]$$

where G, Eads, ZPE, and TS are the free energy, total energy from DFT calculations, zero-point energy, and entropic contributions, respectively.



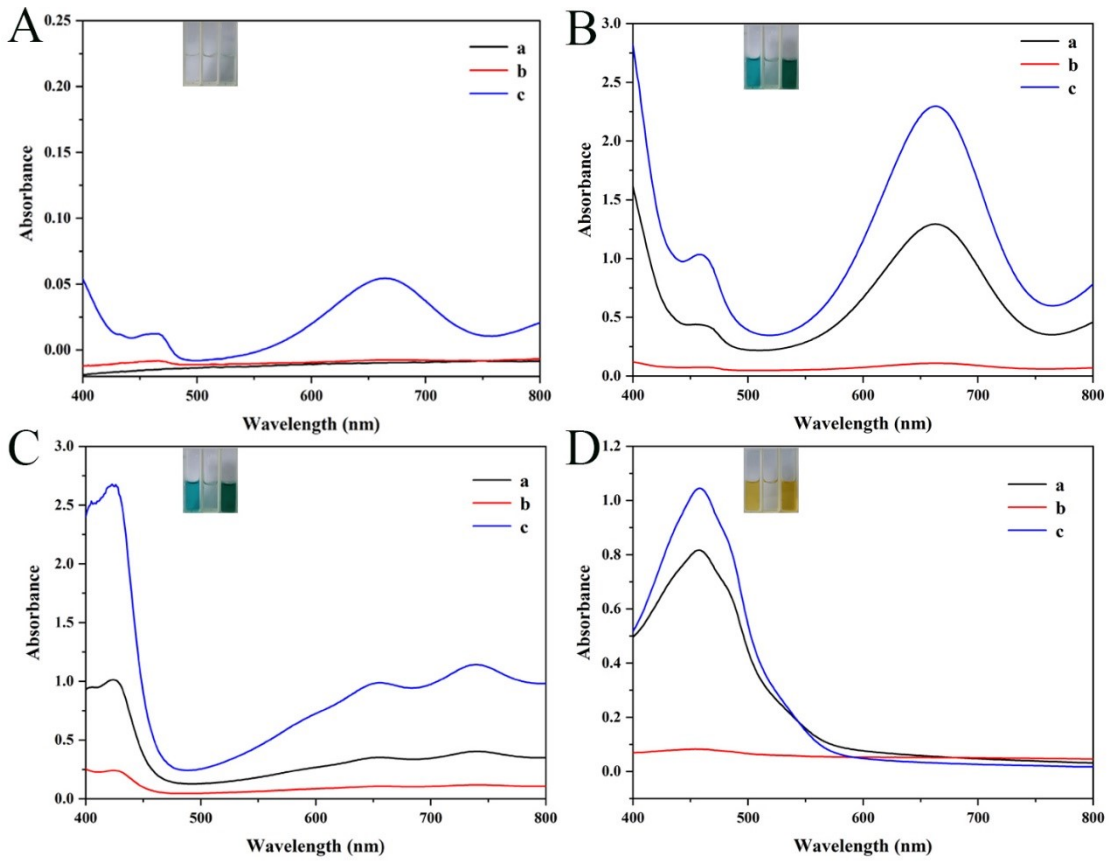


Figure S2. (A) Ultraviolet visible absorption spectrum: (a)TMB,(b)H_2O_2,(c)TMB+H_2O_2. **(B)** Ultraviolet visible absorption spectrum: (a)MIL-88B (Fe)+TMB+H_2O_2(10 mM), (b)MIL-88B (Ni) +TMB+H_2O_2, (c)MIL-88B (Fe, Ni)+TMB+H_2O_2. **(C)** Ultraviolet visible absorption spectrum: (a)MIL-88B (Fe)+ABTS+H_2O_2, (b)MIL-88B (Ni)+ABTS+H_2O_2, (c)MIL-88B (Fe, Ni)+ABTS+H_2O_2. **(D)** Ultraviolet visible absorption spectrum: (a)MIL-88B (Ni)+POD+H_2O_2, (b)MIL-88B (Fe)+POD+H_2O_2,(c)MIL-88B (Fe, Ni)+POD+H_2O_2.

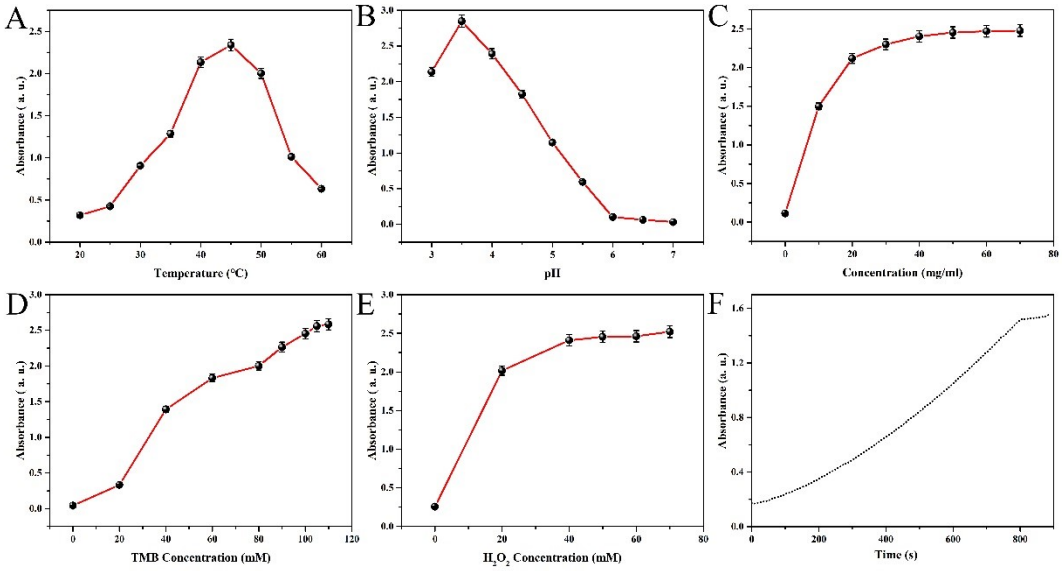


Figure S3. Optimization of peroxidase activity conditions for MIL-88B (Fe, Ni): **(A)** Temperature. **(B)** PH. **(C)** MIL-88B (Fe, Ni) addition amount. **(D)** And **(E)** the amount of TMB and H_2O_2 added. **(F)** Reaction time.

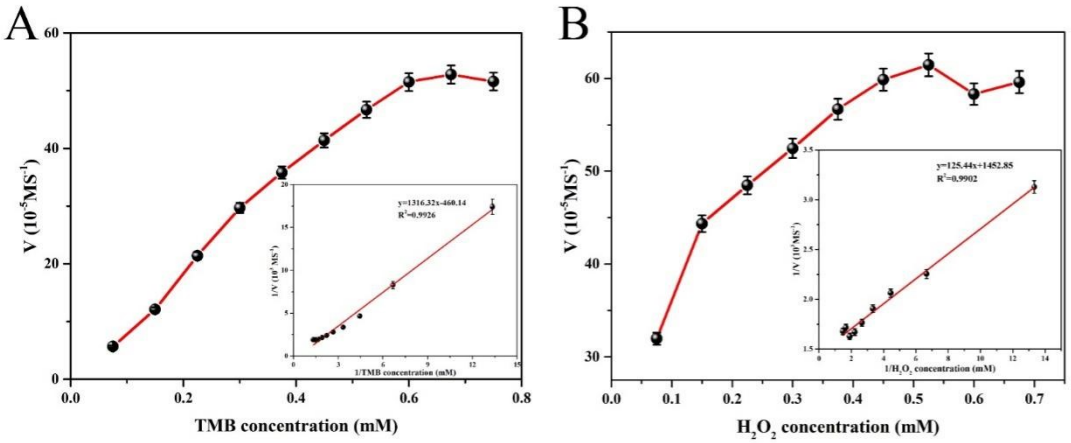


Figure S4. Steady state kinetics of MIL-88B (Fe, Ni) using TMB **(A)** and H_2O_2 **(B)** as substrates.

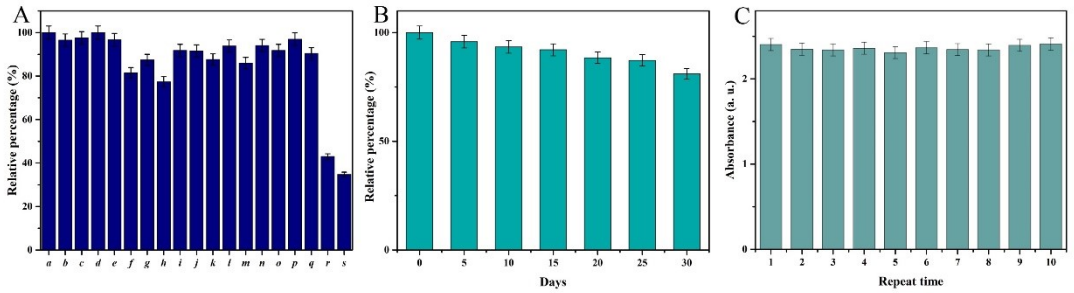


Figure S5. (A) 50 μL MIL-88B (Fe, Ni) (1mg/mL) +100 μL TMB (5 mmol/L) +50 μL H_2O_2 (10 mmol/L) at 45°C: (a) blank, (b) ciprofloxacin, (c) furatone hydrochloride , (d) defoxamycin, (e) formeczin, (f) Atrazine, (g) furacillin, (h) carbendazim, (i) putrescine, (j) glyphosate, (k) histidine, (l) glutamic acid, (m) tryptophan, (n) Pb^{2+}, (o) Cr^{2+}, (p) Cd^{2+}, (q) Ag^{+}, (r) doxycycline hydrochloride, (s) methycline hydrochloride enoxymycin. **(B)** Reproducibility of MIL-88B (Fe, Ni)+TMB+H_2O_2 system. **(C)** Stability of MIL-88B (Fe, Ni)+TMB+H_2O_2 system within 30 day.

Table S1. Distribution Chart Total Spectrum.

element	Line Type	k factor	k factor type	absorption correction	Wt%	Wt% Sigma	At%
C	K linear system	1.864	theory	1.00	37.99	0.68	61.98
N	K linear system	2.425	theory	1.00	0.00	0.00	0.00
O	K linear system	1.444	theory	1.00	18.69	0.38	22.89
Cl	K linear system	1.194	theory	1.00	0.45	0.07	0.25
Fe	K linear system	2.314	theory	1.00	33.72	0.53	11.83
Ni	K linear system	2.747	theory	1.00	9.14	0.34	3.05
total：					100.00		100.00

Table S2. Comparison of the steady-state kinetic parameters for the peroxidase-like activity MIL-88B (Fe, Ni) and other nanozymes.

Materials	**substrate**	**K_m(mmol/L)**	**references**
MIL-88B (Fe, Ni)	TMB H_2O_2	0.6950 0.0767	**This work**
HRP	TMB H_2O_2	0.430 3.700	6
FeCDs	OPD H_2O_2	19.45 0.28	7

C-dots/NiAl-LDH	TMB H_2O_2	0.34 4.72	8
$CePO_4$-CeO_2	TMB	0.263	9
Mo-CQDs	TMB H_2O_2	0.38 0.05	10

Table S3. Analytical performance of MIL-88B (Fe, Ni)/TMB/H_2O_2 catalytic colorimetric sensor for the detection of MET and DOX in water and soil.

Sample	**Added (μM)**	**Determined(μM)**	**RSD (n=3,%)**	**Recovery(n=3)**
MET	0	10.63	1.82	-
	14	24.89	2.23	102.85
	35	46.13	2.37	99.35
	42	53.88	4.32	97.28
DOX	0	12.35	1.35	-
	7	19.32	2.04	99.57
	17.5	30.03	2.26	101.3

	25.5	38.64	2.20	103.1

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