Supporting information:

Reversible inhibition of the oxidase-like activity of Fe single-atom nanozymes for drug detection

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Materials

Zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$), 1,10-Phenanthroline monohydrate, 4-Acetamidophenol (AMP) and 3,3,5,5-tetramethylbenzidine (TMB) were purchased from Aladdin. Iron (Ⅱ) phthalocyanine (FePc) was obtained from Energy Chemical (Shanghai) Co., Ltd. Sodium chloride (NaCl), ethanol, Dimethyl sulfoxide (DMSO) and hydrochloric acid were bought from XiLong SCIENTIFIC. Co., Ltd. Paracetamol tablets were bought from Fuzhou Neptunus Fuyao Pharmaceuticals Co., Ltd. All the chemicals were used without further purification. Ultrapure water (≥18.2 MΩ cm) was used throughout the study.

Apparatus and characterization

TEM images were obtained with a HITACHI 600 transmission electron microscope operated at 100 kV. SEM images were collected via a Zeiss Gemini Sigma 300 SEM instrument. UV-vis absorption measurements were carried out on an Agilent Cary 60 (Varian) UV-vis-near-infrared (NIR) spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMKII (VG Co., UK) spectrometer with an Al Kα excitation source. X-ray diffraction (XRD) characterization was carried out by D8 ADVANCE (Bruker, Germany) diffractometer using Cu K radiation (λ=1.54 Å). Aberration-corrected high angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images were taken using an FEI Themis Z instrument equipped with a spherical aberration corrector. X-ray absorption fine structure spectra (XAFS) were obtained at 1W1B-XAFS station at Beijing Synchrotron Radiation Facility (P. R. China). Raman spectra were recorded on a LabRAM HR800 confocal Raman microscope (Horiba Jobin Yvon) with a laser excitation of 532 nm. Electron paramagnetic resonance (EPR) experiments were carried out on Bruker EMXnano EPR spectrometer.

Supporting Figures

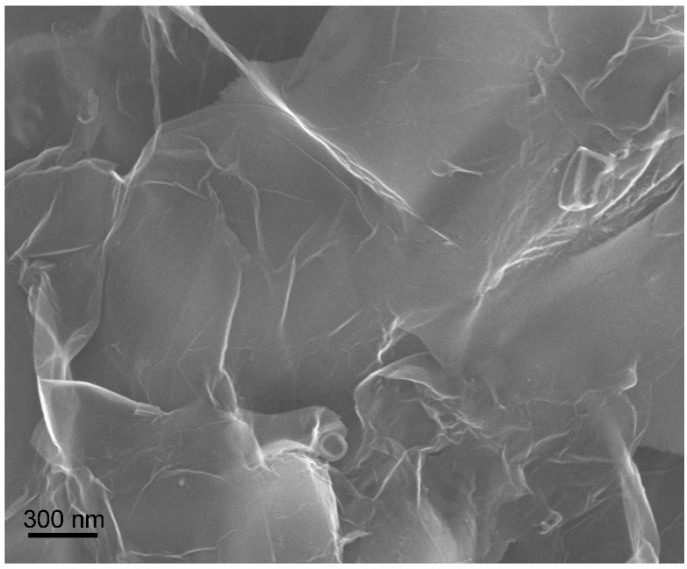

Figure S1. SEM image of Fe-SANs.

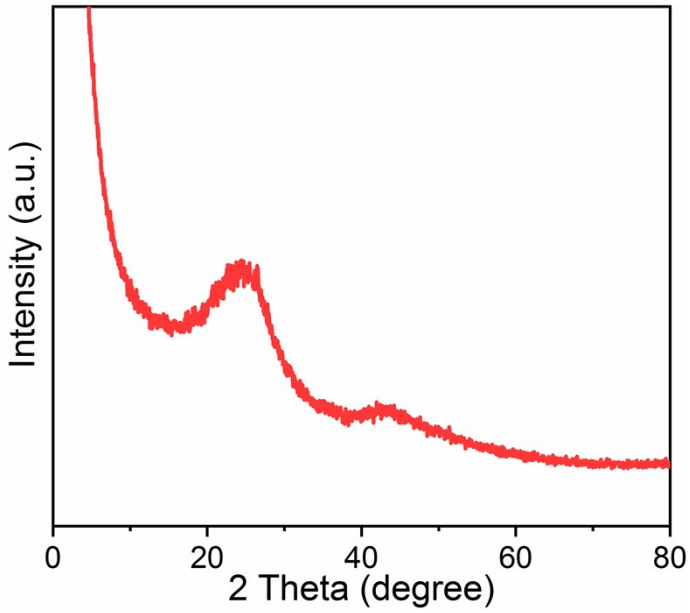

Figure S2. XRD patterns of Fe-SANs.

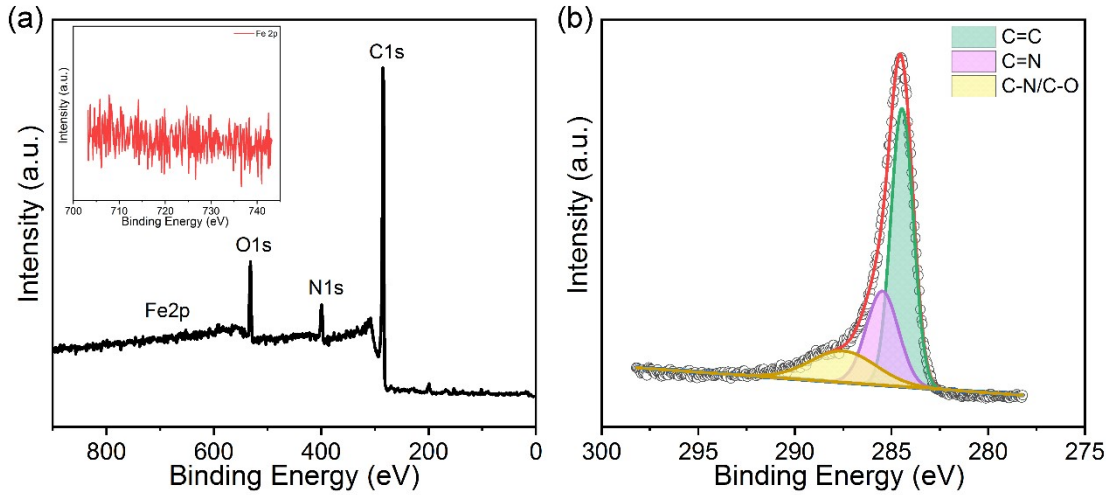

Figure S3. (a) XPS survey scan (inset: Fe 2p spectra) and (b) C 1s spectra of Fe-SANs.

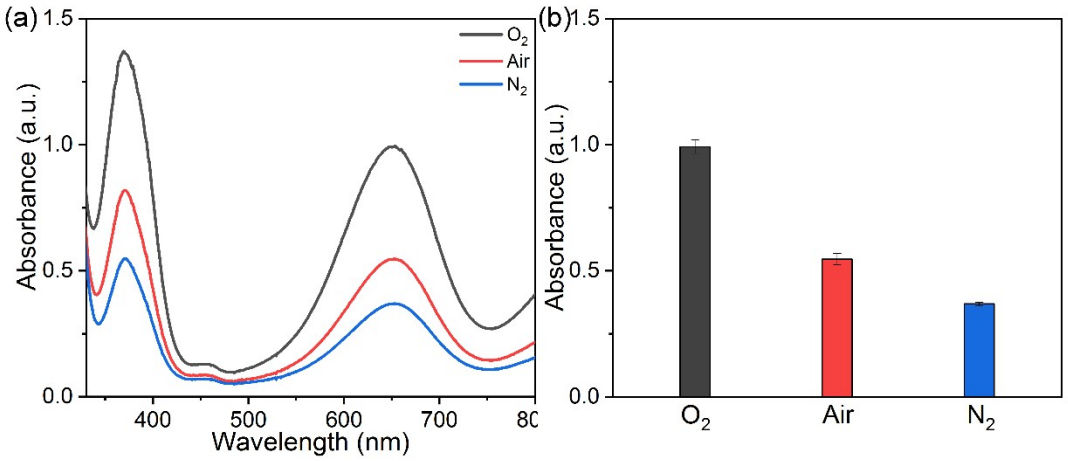

Figure S4. (a) UV-vis absorption spectra and (b) absorbance at 652 nm of TMB in the presence of Fe-SANs in O_2, N_2 and air-saturated buffer.

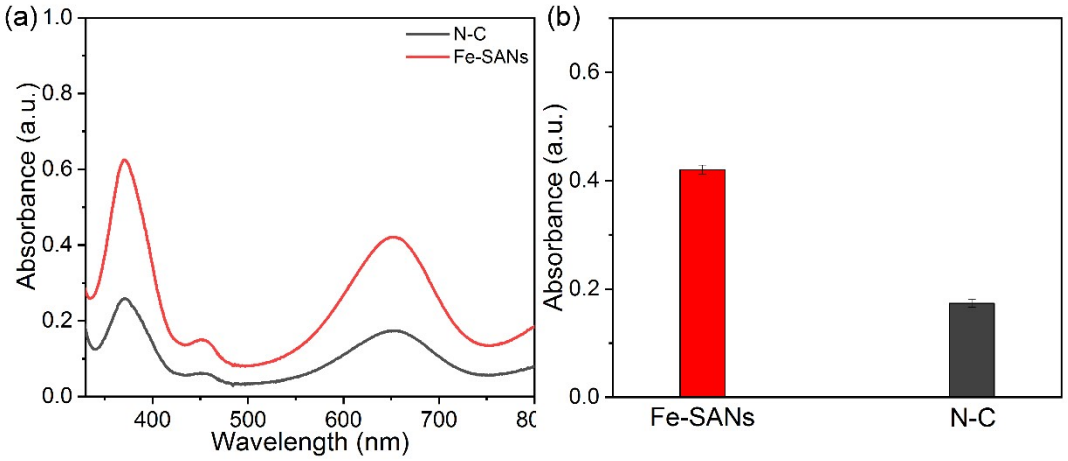

Figure S5. (a) UV-vis absorption spectra and (b) absorbance at 652 nm of TMB in the presence of Fe-SANs and N-C nanosheets in air-saturated buffer.

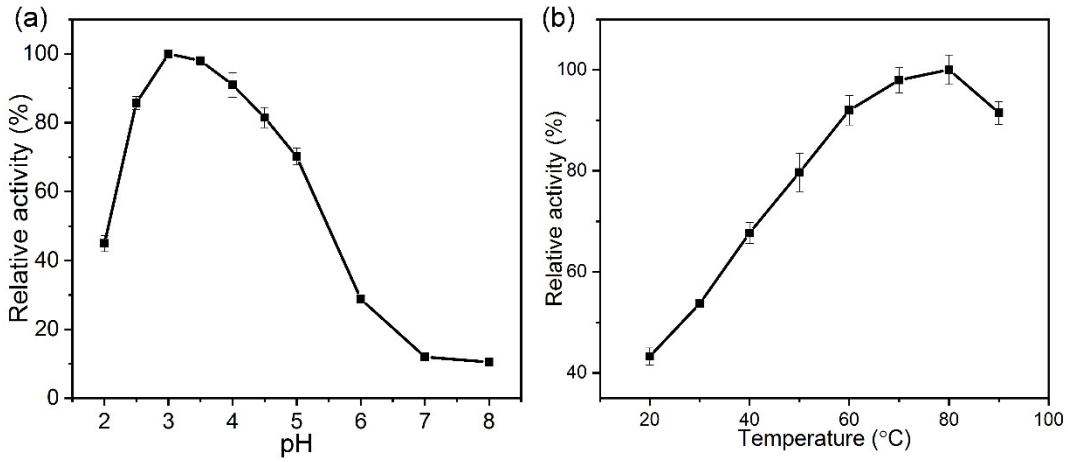

Figure S6. The relative activity of Fe-SANs at different (a) pH and (b) temperatures.

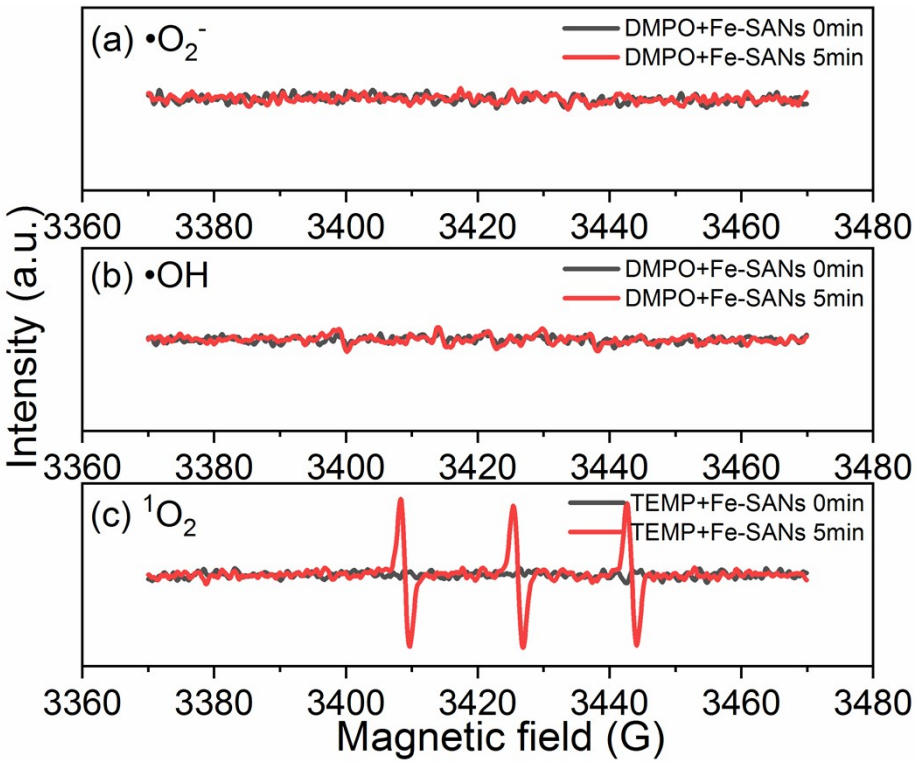

Figure S7. The ESR spectra of (a) DMPO/Fe-SANs aqueous suspension, (b) DMPO/Fe-SANs in methanol and (c) TEMP/ Fe-SANs aqueous suspension.

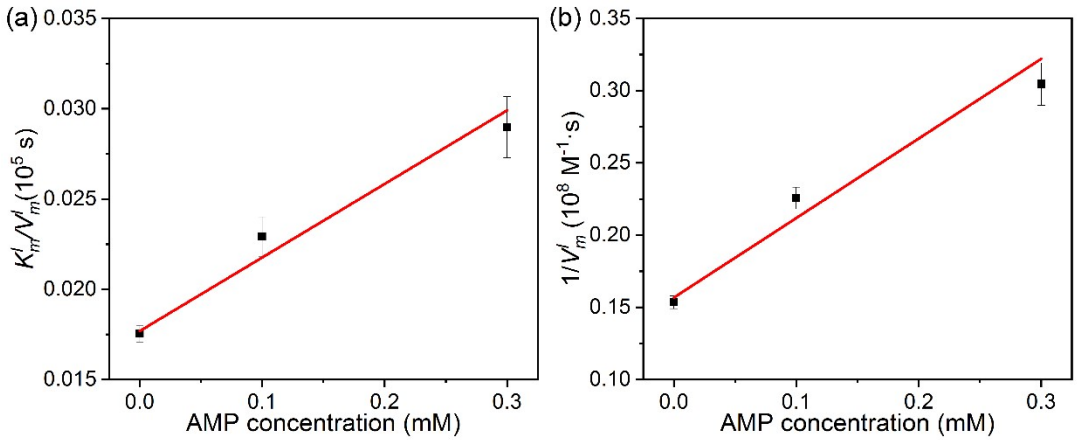

Figure S8. (a) The slopes (K_m^I/V_m^I) and (b) intercepts ($1/V_m^I$) of Lineweaver-Burk plots of Fe-SANs for TMB at different AMP concentrations.

Table S1. Comparison of the kinetic parameters of Fe-SANs with other iron-based nanozymes.

Sample	[E] (M)	K_m (mM)	V_m ($\times10^{-8}$M s^{-1})	k_{cat} (s^{-1})	k_{cat}/K_m (mM^{-1} s^{-1})	Ref
Fe-SANs	5.00×10^{-8}	0.114	6.51	1.30	11.40	This work
FeN_5 SA/CNF	1.07×10^{-6}	0.148	75.80	0.71	4.79	1
Fe SAEs	1.07×10^{-6}	0.130	2.25	0.02	0.16	2
Fe-N/C	7.36×10^{-6}	0.940	59.80	0.08	0.09	3
Fe-N/C	6.79×10^{-5}	0.205	54.10	7.97×10^{-3}	0.04	4
Pero-nanozysome	1.21×10^{-5}	0.550	4.53	3.76×10^{-3}	0.01	5
Fe-N-C SACs		1.810	0.06			6
Fe-N/C-CNTs		0.620	52.60			7
Fe-N-C-400		0.269	33.80			8
Fe_3C/N-		0.225	32.50			9

C				
FeBi-NC	0.210	7.00		10
MOF(Co/2Fe)	0.199	0.39		11

Table S2. Kinetic parameters of Fe-SANs toward TMB at different AMP concentration.

AMP concentration (mM)	K_m (mM)	V_m ($\times 10^{-8}$M s^{-1})
0	0.114	6.51
0.1	0.102	4.43
0.3	0.095	3.28

Table S3. Determination of AMP in paracetamol tablets.

Original amount (mM)	Added (mM)	Found (mM)	Recovery (%)	RSD (%)
0.099	0.125	0.214	92.0	3.4
	0.175	0.292	110.3	5.7
	0.275	0.389	105.5	1.4

References:

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